REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
01-12-2003	Technical Paper	

4. TITLE AND SUBTITLE

1-Alkyl-4-Amino-1,2,4-Triazolium Salts, New Families of Ionic Liquids

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Greg W. Drake, Tommy Hawkins (AFRL/PRSP); Kerri Tollison (ERC); Leslie Hall, Ashwani Vij (AFRL/PRSP); Sarah Sobaski (ERC)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-PR-ED-TP-2003-307

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-PR-ED-TP-2003-307

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

For an American Chemical Society (ACS) monograph series. Supplemental Section of X-ray and spectral data is accessible from the ACS website, not provided here.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A	27	19b. TELEPHONE NUMBER (include area code) (661) 275-5015

1-Alkyl-4-Amino-1,2,4-Triazolium Salts, New Families of Ionic Liquids

Greg W. Drake[#]; Tommy Hawkins[#]; Kerri Tollison*; Leslie Hall[#]; Ashwani Vij[#], Sarah Sobaski*

[#]Space and Missile Propulsion Division
Propellants Branch
and
*ERC, Incorporated
10 East Saturn Boulevard
Air Force Research Laboratory
Edwards Air Force Base, CA 93524-7680

Abstact: New classes of ionic liquids based upon the halide and nitrate salts of 1-alkyl substituted-4-amino-1,2,4-triazolium cations (n-alkyl = methyl -decyl, isopropyl, allyl, and methylcylcopropyl) have been synthesized, characterized by vibrational spectra, multinuclear nmr, elemental analysis, and DSC studies. Single crystal x-ray diffraction studies were carried out on 1-isopropyl-4-amino-1,2,4-triazolium bromide, 1-ethyl-4-amino-1,2,4-triazolium bromide, 1-n-propyl-4-amino-1,2,4-triazolium bromide, 1-n-hexyl-4-amino-1,2,4-triazolium bromide, and 1-n-heptyl-4-amino-1,2,4-triazolium bromide, as well as 1-isopropyl-4-amino-1,2,4-triazolium nitrate and 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate. The details of similarities, differences, and the effects of strong hydrogen bonding in the all of the structures will be discussed.

Introduction

The field of ionic liquids is a rapidly growing area of interest in many areas of chemistry.[1-7] Ionic liquids were originally investigated as possible replacement electrolytes in battery applications by pioneering efforts of Wilkes and Hussey.[8] With the discovery of water stable systems[9, 10], recent efforts have been rapidly expanding the boundaries of applications for ionic liquids rather than on the materials themselves. Much of the chemistry is based upon N-N'-disubstituted imidazolium cations paired with anions such as hexafluorophosphate[10], tetrafluoroborate[9], and triflate[5, 6] anions. Ionic liquids have found a wide array of applications from reaction media[3, 5, 6, 7, 11-18], in separation sciences[5, 6, 19-21], and in many kinds of catalyses reactions[5, 6, 22-27].

At the Air Force Research Laboratory, we have been investigating low melting salts and have found that the behavior is not restricted to the well-known 1,3-di-alkyl substituted imidazolium and 1-alkyl-pyridinium cation based salts. In efforts at identifying additional classes of low melting salts, other five-membered azole rings were considered as possibly being substituted in a 1,4 conformation, similar to that found in the related 1,3-disubstituted imidazolium cation systems, might lead to similar ionic liquid properties. Examples of 1,4-disubstituted-triazolium salts have been known for quite sometime[28-30] and recently, Shreeve[31-33] has demonstrated this behavior with a large new family of ionic liquids based on fluoro-alkylated 1,4-disubstituted-1,2,4-triazolium cations. Extending the premise that asymmetric 5-membered heterocyclic cations will have poor packing in three-dimensional space, which would result in new classes of low melting materials, we have found this behavior in a similarly shaped heterocycle, 4-amino-1,2,4-triazole. The 4-amino-1,2,4-triazole ring system has a much higher nitrogen content as well as a non-basic amine group, which we felt would make for unusual physical properties. As is often true in many research arenas our predecessors have often demonstrated chemistries for materials in completely different scientific pursuits. However, no one has considered the thought of this heterocycle as an ionic liquid building block with the 4-amino-1,2,4-triazolium cationic species serving as the heterocyclic platform. There are several brief reports throughout the last several decades describing various 1-substituted-4-amino-1,2,4-triazolium salts[34-39], and recently former Soviet Union research groups have produced interesting examples such as 1-substituted-4-amino-1,2,4-triazolium nitrates using the powerful amination reagent, picryloxyamine, in reactions with 1-R-1,2,4-triazoles[40, 41] and subsequent N-amino nitration forming highly unusual 1-R-substituted-4-nitramino-1,2,4-triazole zwitterions[42, 43].

We have been able to synthesize and characterize a large new family of low melting salts based upon 1-substituted-4-amino-1,2,4-triazolium cation species as halide and nitrate salts through simple reactions with commercially available materials in high yields and purities. New species include 1-n-alkyl (methyl-decyl, isopropyl, 1-methylcyclopropyl-, and 2-propenyl)-1-substituted-4-amino-1,2,4-triazolium

cations. The syntheses, physical properties, spectral data, as well as several x-ray diffraction crystal structures of the salts will be discussed.

Experimental

The starting materials, 4-amino-1,2,4-triazole, methyl iodide, n-alkyl bromides (ethyl-decyl), allyl bromide, and bromomethylcyclopropane were purchased from Aldrich Chemical Company, Inc, and their purities checked by ^{1}H and ^{13}C NMR prior to use. Methanol, CH_3OH; Ethanol, CH_3CH_2OH; and 2-Propanol, $(CH_3)_2CH$-OH, (ACS reagent grade; distilled from sodium metal), and acetonitrile, CH_3CN (HPLC grade; distilled from calcium hydride) were purchased from Aldrich Chemical Company, and all solvents were degassed using a liquid nitrogen freeze-thaw vacuum procedure. Diethyl ether was dried through a pre-activated alumina column prior to use. All solvents were stored inside glass vessels, which were sealed with teflon screw-cap plugs, and were equipped with #15 O-ring fittings. Infrared spectra were recorded as KBr disks (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer from 4000-400 cm^{-1}. Raman spectra were recorded in pyrex melting point capillaries on Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in d_6-dmso in 5mm nmr tubes inside a drybox, and the ^{1}H and ^{13}C spectra recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield™ NMR. Thermal analyses were carried out in hermetically sealed, coated aluminum pans on a Thermal Analyst 200, Dupont Instruments 910 Differential Scanning Calorimeter. DSC samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with 10 mL per minute of nitrogen gas purge during heating cycles. Elemental analyses were carried out on a Perkin Elmer Series II CHNS/O Analyzer 2400 elemental analysis instrument equipped with AD6 Autobalance and by Desert Analytics, Inc. of Tucson, AZ. Densities were measured using helium displacement techniques in a calibrated cell using a Quantachrome Ultrapycnometer 1000 instrument. The synthesis of 1-n-butyl-4-amino-1,2,4-triazolium bromide was described previously.[37]

1-methyl-4-amino-1,2,4-triazolium iodide (I): 4-amino-1,2,4-triazole, 5.1833g., 61.6 mmoles, was weighed out and placed in a 250 ml round-bottomed flask with a Teflon stir bar. Isopropyl alcohol, 200ml, was added and the mixture stirred for a short period of time to completely dissolve the 4-amino-1,2,4-triazole. Methyl iodide, 26.5143 g., 186 mmoles, was then added to the vigorously stirred solution. The flask was then protected from light with a black bag, and stirred for seven days at ambient temperature. At the end of this time an additional 1.50g of methyl iodide was added and the reaction mixture stirred for five additional days. The solution was pale yellow with white precipitate in the bottom of the flask. The precipitate was filtered and washed four aliquots, 50 ml each, of cold isopropyl alcohol, followed by four washings, 50 ml each, of cold diethyl ether. The white powder was then transferred to a preweighed Schlenk flask and evacuated overnight to leave 10.1840 g, 45.0 mmoles of 1-methyl-4-amino-1,2,4-triazolium iodide. Melting point 98°C, DSC onset beginning at 136°C. ^{1}H NMR(d_6-dmso): 4.024 (singlet, area 3.067), 6.938 (singlet, area 1.661), 9.161 (singlet, area 0.932), 10.115 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 39.107, 143.002, 145.109. Elemental analysis: %C: 15.94 (theory); 16.19 (found); %H: 3.12 (theory); 3.04 (found); %N: 24.79 (theory); 24.59 (found).

1-ethyl-4-amino-1,2,4-triazolium bromide (II): A 500 ml round-bottom flask equipped with an overhead stirrer was charged with 10.00 g. of 4-amino-1,2,4-triazole and 200 ml of acetonitrile. Ethyl bromide, 45 ml, 65.0 g., was added to the vigorously stirred reaction mixture. The reaction was stirred for 8 days at ambient temperature at which time, thin layer chromatography showed that all of the 4-amino-1,2,4-triazole had been consumed. The resultant solution was then rotary evaporated down leaving a colorless ionic liquid which slowly crystallized. The solid material was heated to 60°C for 5 hours under high vacuum, whereupon it melted, lost the remaining solvent, and re-solidified as highly crystalline 1-ethyl-4-amino-1,2,4-triazolium bromide in essentially quantitative yield and high purity, 22.94 g., 117 mmoles. Melting point: 63-67°C; DSC onset: 150°C. ^{1}H NMR (d_6-dmso): 1.402, 1.420, 1.438 (triplet, area 3.000); 4.359, 4.377, 4.395, 4.413 (quartet, area 2.003); 7.084 (broad singlet, area 1.648); 9.202 (singlet, area 0.959); 10.325 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 13.768, 47.335, 142.289, 145.114. Elemental analysis: %C: 24.95 (theory); 24.73 (found); %H: 4.74 (theory); 4.73 (found); %N: 29.21(theory); 29.09 (found).

1-n-propyl-4-amino-1,2,4-triazolium bromide (III): In the typical manner as cited for **II** above, 10.005 g., 118 mmoles, of 4-amino-1,2,4-triazole was reacted with 1-bromopropane, 58.865g., 478 mmoles in

acetonitrile at 50°C, yielding highly crystalline 1-n-propyl-4-amino-1,2,4-triazolium bromide, 23.9584 g, 115 mmoles. Melting point: 63°C; DSC onset 145°C. ^{1}H NMR (d_6-dmso): 0.806, 0.823, 0.836 (triplet, area 3.000); 1.818, 1.834 (broad multiplet, area 2.013); 4.362, 4.373 (broad multiplet, area 1.999); 7.126 (broad singlet, area 1.816); 9.244 (singlet, area 0.928); 10.440 (singlet, area 0.957). ^{13}C NMR (d_4-MeOH): 11.051, 23.313, 55.538, 144.586, 146.908. Elemental analysis, %C: 29.00 (theory); 28.96 (found); %H: 5.35 (theory); 5.46 (found); %N: 27.06 (theory); 27.48 (found).

1-isopropyl-4-amino-1,2,4-triazolium bromide (IV): In the manner of **II** above, 10.122 g., 120 mmoles, of 4-amino-1,2,4-triazole was reacted at 50°C with 2-bromopropane 58.560 g., 476 mmoles yielding on work-up, 1-isopropyl-4-amino-1,2,4-triazolium bromide, 17.421 g., 84 mmoles. Melting point: 92°C; DSC onset 145°C. ^{1}H NMR (d_6-dmso): 0.461, 0.472, 0.557, 0.576 (complex multiplet, relative area 4.000); 1.273, 1,283, 1.293, 1.302, 1.313, 1.320, 1.332 (complex multiplet, area 0.992); 4.261, 4.279 (doublet, area 2.032); 7.088 (broad singlet, area 1.309); 9.231 (singlet, area 0.971); 10.412 (singlet, area 1.309). ^{13}C NMR (d_6-dmso): 3.849, 10.082, 56.162, 142.150, 145.179. Elemental analysis: %C: 32.89 (theory); 32.73 (found); %H: 5.06 (theory); 5.07 (found); %N: 25.57 (theory); 25.27 (found).

1-(2-propenyl)-4-amino-1,2,4-triazolium bromide (V): In the manner of **II** above 4-amino-1,2,4-triazole, 10.000 g., 118 mmoles, was reacted with allyl bromide, 43.10 g, 356 mmoles resulting in 1-allyl-4-amino-1,2,4-triazolium bromide, 12.657 g., 62 mmoles. Melting point: 59-62° C; DSC onset: 130° C. ^{1}H NMR (d_6-dmso): 5.068, 5.288, 5.316, 5.328 5.325 (broad multiplets, area 3.033); 5.993, 5.946, 5.958, 5.974, 5.987, 6.000 (broad multiplet, area 0.890); 7.126 (broad singlet, area 1.962); 9.234 (singlet, area 0.938); 10.426 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 53.736, 120.912, 130.255, 142.572, 145.292. Elemental analysis: %C: 29.29 (theory); 29.37 (found); %H: 4.42 (theory); 4.59 (found); %N: 27.32 (theory); 27.04 (found).

1-methylcyclopropyl-4-amino-1,2,4-triazolium bromide (VI): In the manner of **II** above 4-amino-1,2,4-triazole 3.2154 g., 38.2 mmoles, was reacted with bromomethylcyclopropane, 10.7539 g., 79.6 mmoles, yielding 1-methylcyclopropyl-4-amino-1,2,4-triazolium bromide, 4.8167 g., 22 mmoles. Melting point: 71-73°C; DSC onset: 150° C. ^{1}H NMR (d_6-dmso): 0.461, 0.472, 0.557, 0.576 (complex multiplet, area 4.000); 1.27, 1,283, 1.293, 1.302, 1.313, 1.320, 1.332 (complex multiplet, area 0.992); 4.261, 4.279 (doublet, area 2.032); 7.088 (broad singlet, area 1.309); 9.231 (singlet, area 0.971); 10.412 (singlet, area 1.309). ^{13}C NMR (d_6-dmso): 3.849, 10.082, 56.162, 142.150, 145.179. Elemental analysis: %C: 32.89 (theory); 32.73 (found); %H: 5.06 (theory); 5.07 (found); %N: 25.57 (theory); 25.27 (found).

1-n-pentyl-4-amino-1,2,4-triazolium bromide (VII): In the manner of **II** above 4-amino-1,2,4-triazole, 2.000 g., 23.7 mmoles, was reacted with n-pentyl bromide 7.22 g., 47.8 mmoles, resulting in 1-n-pentyl-4-amino-1,2,4-triazolium bromide, 4.4737 g., 19.0 mmoles. Melting point: 54°C; DSC onset: 130°C. ^{1}H NMR (d_6-dmso): 0.819, 0.838, 0.855, 0.880, 0.897 (broad multiplet, area 2.321); 1.180, 1.194, 1.202, 1.215, 1.233, 1.249, 1.261, 1.278, 1.296, 1.313 (complex multiplet, area 3.438); 1.788, 1.805, 1.823, 1.842, 1.859 5.994 (complex multiplet, area 1.889); 4.343, 4.361, 4.378 (triplet, area 2.000); 7.041 (broad singlet, area 2.121); 9.217 (singlet, area 0.914); 10.357 (singlet, area 0.996). ^{13}C NMR (d_6-dmso): 13.691, 21.423 , 27.453, 27.728, 51.675, 142.602, 145.196. Elemental analysis: %C: 35.76 (theory); 35.25 (found); %H: 6.43 (theory); 6.45 (found); %N: 23.83 (theory); 24.25 (found).

1-n-hexyl-4-amino-1,2,4-triazolium bromide(VIII): In a similar method to that used for **II** above, 2.000 g., 23.7 mmoles of 4-amino-1,2,4-triazole was reacted with n-hexyl bromide 8.080 g., 48.9 mmoles, at 60°C for 40 hours, resulting 4.924 g., 19.7 mmoles, of 1-n-hexyl-4-amino-1,2,4-triazolium bromide. Melting point: 76°C; DSC onset: 130 C. ^{1}H NMR (d_6-dmso): 0.842, (broad singlet, area 2.377); 1.253 (broad singlet, area 5.597); 1.825 (broad singlet, area 1.757); 4.371 (broad singlet, area 2.000); 7.082 (broad singlet, area 1.966); 9.236 (singlet, area 0.859); 10.363 (singlet, area 0.927). ^{13}C NMR (d_6-dmso): 13.797, 21.821, 24.985, 27.993, 30.461, 51.962, 142.587, 145.182. Elemental analysis: %C: 38.57 (theory); 38.32 (found); %H: 6.43 (theory); 6.45 (found); %N: 22.49 (theory); 22.88 (found).

1-n-heptyl-4-amino-1,2,4-triazolium bromide(IX): In the manner stated in **II** above, 2.000 g., 23.7 mmoles, of 4-amino-1,2,4-triazole was reacted with n-heptyl bromide 10.650 g., 59.1 mmoles, at 60°C for 40 hours, resulting 5.7460 g., 21.7 mmoles, of 1-n-heptyl-4-amino-1,2,4-triazolium bromide. Melting point:

94°C; DSC onset: 130°C. ^{1}H NMR (d_6-dmso): 0.807, 0.824, 0.840 (triplet, area 3.000); 1.221, 1.235, 1.244 (broad multiplet, area 8.966); 1.797, 1.813, 1.830 (multiplet, area 2.146); 4.346, 4.364, 4.381 (triplet, area 2.358); 7.090 (broad singlet, area 2.122); 9.220 (singlet, area 1.059), 10.375 (singlet, area 1.094). ^{13}C NMR (d_6-dmso): 13.587, 21.927, 25.270, 27.941, 28.046, 30.959, 51.672, 142.560, 145.153. Elemental analysis: %C: 41.07 (theory); 41.24 (found); %H: 7.28 (theory); 7.05 (found); %N: 21.29 (theory); 21.13 (found).

1-n-octyl-4-amino-1,2,4-triazolium bromide (X): In essentially the same manner as in II above, 2.000 g., 23.7 mmoles, of 4-amino-1,2,4-triazole was reacted with n-octyl bromide 9.790 g., 50.7 mmoles, at 60°C for 40 hours, yielding 5.4768 g., 19.7 mmoles, of 1-n-octyl-4-amino-1,2,4-triazolium bromide. Melting point: 81°C; DSC onset: 130°C. ^{1}H NMR(d_6-dmso): 0.815(broad singlet), 1.227 (broad singlet), 1.806 (broad singlet), area of all three peaks 17.211), 4.369 (broad singlet, area 2.000), 7.112 (broad singlet, area 1.993), 9.225 (singlet, area 0.880), 10.404 (singlet, area 0.868). ^{13}C NMR (d_6-dmso): 13.848, 22.000, 25.319, 28.055, 28.257, 28.405, 31.102, 51.660, 142.525, 145.117. Elemental analysis: %C: 43.32 (theory); 43.57 (found); %H: 7.64 (theory); 7.56(found); %N: 20.21(theory); 20.16(found).

1-n-nonyl-4-amino-1,2,4-triazolium bromide (XI): As in II above, 2.000 g., 23.7 mmoles, of 4-amino-1,2,4-triazole was reacted with n-nonyl bromide 12.319 g., 59.1 mmoles, at 60°C for 40 hours, yielding 6.3680 g., 21.7 mmoles, of 1-n-nonyl-4-amino-1,2,4-triazolium bromide. Melting point: 81°C; DSC onset: 130°C. ^{1}H NMR (d_6-dmso): 0.823, 0.839, 0.854 (triplet, area 3.266); 1.230 (broad, 13.571); 1.827, 1.843 (broad, area 2.165); 4.363, 4.380, 4.397 (triplet, area 2.191); 7.090 (broad singlet, area 1.873), 9.24 (singlet, area 1.069); 10.397 (singlet, area 1.111). ^{13}C NMR (d_6-dmso): 13.913, 22.072, 25.363, 28.089, 28.346, 28.590, 28.758, 31.242, 51.698, 53.865, 142.580, 145.166. Elemental analysis: %C: 45.37 (theory); 45.61 (found); %H: 7.96 (theory); 8.06 (found); %N: 19.24 (theory); 19.21 (found).

1-n-decyl-4-amino-1,2,4-triazolium bromide (XIII): As in II above 2.000 g., 23.7 mmoles, of 4-amino-1,2,4-triazole was reacted with n-decyl bromide 10.770 g., 48.7 mmoles at 60°C for 40 hours, yielding 6.3227 g., 20.7 mmoles, of 1-n-decyl-4-amino-1,2,4-triazolium bromide. Melting point: 90°C; DSC onset: 135°C. ^{1}H NMR (d_6-dmso): 0.821, 0.838, 0.853 (triplet, area 2.621), 1.226 (broad singlet, area 15.002) 1.820, 1.836 (broad doublet, area 2.039), 4.334, 4.351, 4.368 (triplet, area 2.000), 7.055 (broad singlet, area 1.887), 9.212 (singlet, area 0.984), 10.321 (singlet, area 1.027). ^{13}C NMR (d_6-dmso): 13.916, 22.064, 25.348, 28.042, 28.307, 28.648, 28.785, 28.869, 31.250, 51.700, 142.592, 145.176. Elemental analysis: %C: 47.22 (theory); 47.31 (found); %H: 8.25 (theory); 8.04 (found); %N: 18.35 (theory); 18.40 (found).

1-ethyl-4-amino-1,2,4-triazolium nitrate (XIV): In a 250 mL beaker, 1-ethyl-4-amino-1,2,4-triazolium bromide, 3.9543 g., 20.5 mmoles was dissolved of methanol. In a 1 liter round bottomed flask, silver nitrate, 3.4794 g., 20.5 mmoles, was dissolved in 250 ml of methanol at 60°C in a darkened room. The methanolic solution of 1-ethyl-4-amino-1,2,4-triazolium bromide was slowly added with a disposable pipette over a 10 minute period to the vigorously stirred silver nitrate solution (which had been removed from the heating bath), and after the addition was completed the reaction mixture was stirred until it cooled to room temperature (30 minutes). It was then filtered through a plug of celite, the flask and celite plug were subsequently washed with fresh aliquots of methanol to insure complete transfer of product through filter. The resultant filtrate was rotary evaporated down to a minimum volume, transferred to a pre-weighed Schlenk flask with fresh methanol (30 ml). The flask was then immersed in a heating bath (60°C) for 16 hours, with frequent agitation to remove all of volatiles resulting in the ionic liquid product of 1-ethyl-1,2,4-triazolium nitrate, 3.5467g., 20.2 mmoles, (98%). After the mass was recorded a very small portion of the product salt was added to a concentrated silver nitrate solution, with no cloudiness or precipitation that were observable that would be indicative of bromide anion. Melting point: -50°C; DSC onset: 160°C. ^{1}H NMR (d_6-dmso): 1.410, 1.428, 1.446 (triplet, area 3.000); 4.334, 4.352, 4.370, 4.388 (quartet, area 2.023); 7.016 (singlet, area 1.991); 9.164 (singlet, area 0.961); 10.200 (singlet, area 0.978). ^{13}C NMR (d_6-dmso): 13.834, 47.465, 142.605, 145.366. Elemental analysis: %C: 27.43 (theory); 27.27 (found); %H: 5.17 (theory); 5.55 (found); %N: 39.98 (theory); 39.83 (found).

1-methyl-4-amino-1,2,4-triazolium nitrate (XV): In a similar manner to that used for XIV above, 1-methyl-4-amino-1,2,4-triazolium iodide, 1.3063g., 5.78 mmoles, was reacted with silver nitrate, 0.9825 g., 5.78 mmoles, yielding 1-methyl-4-amino-1,2,4-triazolium nitrate, 0.8925 g., 5.54 mmoles, 95%. Melting point: -54°C; decomposition onset 175°C. ^{1}H NMR(d_6-dmso): 4.051 (singlet, area 2.974); 6.991 (singlet,

area 1.719); 9.079 (singlet, area 0.954); 10.116 (singlet, 0.997). ^{13}C NMR(d_6-dmso): 39.208, 143.584, 145.615. Elemental analysis: %C: 22.22 (theory); 22.06 (found); %H: 4.35 (theory); 4.67 (found); %N: 43.19 (theory); 43.17 (found).

1-n-propyl-4-amino-1,2,4-triazolium nitrate (XVI): In the manner of **XIV** above, 1-n-propyl-4-amino-1,2,4-triazolium bromide, 1.3736 g., 6.63 mmoles, was reacted with silver nitrate, 1.1272 g., 6.63mmoles, resulting in 1-n-propyl-4-amino-1,2,4-triazolium nitrate, 1.2488 g., 6.60 mmoles, 99%. Melting point: 33°C; decomposition onset: 175°C. ^{1}H NMR (d_6-dmso): 0.814, 0.833, 0.851 (triplet, area 3.000); 1.790, 1.808, 1.826, 1.844, 1.862, 1.880 (sextet, area 2.031); 4.286, 4.303, 4.321 (triplet, area 2.043); 7.338 (broad, area 1.957); 9.169 (singlet, area 0.963); 10.225 (singlet, area 0.969). ^{13}C NMR ($d_6$dmso): 10.465, 21.824, 53.437, 143.052, 145.572. Elemental analysis: %C: 31.74 (theory); 31.61 (found); %H: 5.86 (theory); 6.08 (found); %N: 37.02 (theory); 37.24 (found).

1-n-butyl-4-amino-1,2,4-triazolium nitrate (XVII): In the manner of **XIV** above, 1-n-butyl-4-amino-1,2,4-triazolium bromide 1.3063 g., 5.91 mmoles, was reacted with silver nitrate, 1.0041 g., 5.91 mmoles, resulting in 1-n-butyl-4-amino-1,2,4-triazolium nitrate, 1.0510 g., 5.17 mmoles, 88%. Melting point: -50°C (g.t.); decomposition onset 170°C. ^{1}H NMR(d_6-dmso):0.856, 0.874, 0.892 (triplet, area 3.140); 1.213, 1.231, 1.249, 1.268, 1.287, 1.306 (sextet, area 2.047); 1.772, 1.790, 1.809, 1.827, 1.845 (pentet, area 2.092); 4.334, 4.352, 4.369 (triplet, area 2.101); 7.026 (singlet, area 2.061); 9.176 (singlet, area 0.959); 10.253 (singlet, area 1.000). ^{13}C NMR(d_6-dmso): 13.263, 18.731, 30.139, 51.566, 142.883, 145.399. Elemental analysis: %C: 35.46 (theory); 35.75 (found); %H: 6.44 (theory); 6.98 (found); %N: 34.46 (theory); 34.53 (found)

1-isopropyl-4-amino-1,2,4-triazolium nitrate (XVIII): In the manner of **XIV** above, 4.0560 g., 19.6 mmoles, 1-isopropyl-4-amino-1,2,4-triazolium bromide was reacted with silver nitrate 3.3270 g., 19.6 mmoles, yielding on work-up, 1-isopropyl-4-amino-1,2,4-triazolium nitrate, 3.6160 g., 19.1 mmoles, 97%. Melting point: 66°C; DSC onset: 180°C. ^{1}H NMR (d_6-dmso): 1.419, 1.469, 1.474, 1.485, 1.490 (multiplet, area 6.095); 4.741, 4.755, 4.768, 4.785, 4.801, 4.817, 4.834, 4.261, 4.279 (heptet, area 1.000); 6.989 (broad singlet, area 2.000); 9.170 (singlet, area 0.986), 10.244 (singlet, area 0.997). ^{13}C NMR (d_6-dmso): 21.287, 55.420, 141.854, 145.301. Elemental analysis: %C: 31.74 (theory); 31.47 (found); %H: 5.86 (theory); 6.13 (found); %N: 37.02 (theory); 36.61 (found).

1-(2-propenyl)-4-amino-1,2,4-triazolium nitrate (XIX): In the manner of **XIV** above 1-(2-propenyl)-4-amino-1,2,4-triazolium bromide, 1.1348 g., 5.53 mmoles, was reacted with silver nitrate, 0.9976 g., 5.53 mmoles, resulting in 1-allyl-4-amino-1,2,4-triazolium nitrate, 0.9976 g., 5.33 mmoles, 96%. Melting point: -50°C (g.t.); DSC onset: 140°C. ^{1}H NMR (d_6-dmso): 5.004, 5.018 (doublet, area 2.348); 5.321, 5.361, 5.362, 5.386 (multiplet, area 2.273); 5.982, 5.995, 6.008, 6.024, 6.037, 6.050 (multiplet, area 1.092); 7.024 (broad singlet, area 2.000); 9.206 (singlet, area 1.046); 10.217 (singlet, area 1.080). ^{13}C NMR (d_6-dmso): 53.923, 120.985, 130.498, 143.035, 145.545. Elemental analysis: %C: 32.08 (theory); 31.84 (found); %H: 4.84 (theory); 5.15 (found); %N: 37.41 (theory); 37.19 (found).

1-methylcyclopropyl–4-amino-1,2,4-triazolium nitrate (XX): In the manner of **XIV** above 1-methylcyclopropyl-4-amino-1,2,4-triazolium bromide, 1.2467 g., 5.69 mmoles, was reacted with silver nitrate, 0.9666 g., 5.69 mmoles, yielding 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate, 1.1309 g., 5.62 mmoles, 98%. Melting point: 56°C; DSC onset: 185° C. ^{1}H NMR (CD_3CN): 0.411, 0.446, 0.457, 0.461, 0.469, 0.472, 0.484, 0.594, 0.613, 0.630, 0.641, 0.645, 0.650, 0.661, 0.665, 0.667 (complex multiplet, area 4.000); 1.298, 1.305, 1.309, 1.317, 1.325, 1.329, 1.336, 1.344, 1.348, 1.356, 1.368 (complex multiplet, area 1.006); 4.181, 4.200 (doublet, area 2.016), 6.637 (broad singlet, area 2.001); 8.750 (singlet, area 0.890); 10.412 (singlet, area 0.930). ^{13}C NMR (CD_3CN): 4.615, 10.528, 58.173, 143.507, 146.083. Elemental analysis: %C: 35.82 (theory); 35.54 (found); %H: 5.51 (theory); 5.53 (found); %N: 34.81 (theory); 34.66 (found).

1-n-pentyl-4-amino-1,2,4-triazolium nitrate (XXI): In the manner of **XIV** above, 1-n-pentyl-4-amino-1,2,4-triazolium bromide, 1.2505 g., 5.31 mmoles, was reacted with silver nitrate, 0.9024 g., 5.31 mmoles, resulting in 1-n-pentyl-4-amino-1,2,4-triazolium nitrate, 0.9819 g., 4.52 mmoles, 85%. Melting point: 29°C; DSC onset: 180° C. ^{1}H NMR (d_6-dmso): 0.812, 0.830, 0.844 (broad multiplet, area 2.894); 1.208,

1.228, 1.251, 1.269, 1.287 (complex multiplet, area 3.868); 1.807, 1.824, 1.841 (complex multiplet, area 2.048); 4.327, 4.343, 4.359 (triplet, area 2.118); 7.038 (broad singlet, area 2.097); 9.168 (singlet, area 1.022); 10.251 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 13.826, 21.644, 27.655, 27.972, 51.904, 143.021, 145.532. Elemental analysis: %C: 38.70 (theory); 38.77 (found); %H: 6.95 (theory); 6.98 (found); %N: 32.23 (theory); 32.21 (found).

1-n-hexyl-4-amino-1,2,4-triazolium nitrate(XXII): In a manner similar of **XIV** above, 1-n-hexyl-4-amino-1,2,4-triazolium bromide, 1.0561 g., 4.23 mmoles, was reacted with silver nitrate, 0.7195 g., 4.23 mmoles, resulting of 1-n-hexyl-4-amino-1,2,4-triazolium nitrate, 0.9635 g., 4.17 mmoles, 98%. Melting point: -2-0°C; DSC onset: 170° C. ^{1}H NMR (d_6-dmso): 0.820, 0.829, 0.836, (broad multiplet, area 3.378), 1.242 (broad singlet, area 7.011), 1.818 (broad singlet, area 2.130), 4.326, 4.334, 4.343, 4.361 (broad multiplet, area 2.034), 7.040 (broad singlet, area 2.036), 9.157 (singlet, area 1.004), 10.248 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 13.878, 21.999, 25.160, 28.207, 30.652, 51.895, 142.952, 145.450. Elemental analysis: %C: 41.51 (theory); 41.28 (found); %H: 7.40 (theory); 7.93 (found); %N: 30.28 (theory); 30.14 (found).

1-n-heptyl-4-amino-1,2,4-triazolium nitrate(XXIII): In the manner stated in **XIV** above, 1-n-heptyl-4-amino-1,2,4-triazolium bromide, 1.0031 g., 3.81 mmoles, was reacted with silver nitrate, 0.6470 g., 3.81 mmoles, resulting of 1-n-heptyl-4-amino-1,2,4-triazolium nitrate, 0.9115 g., 3.72 mmoles, 97%. Melting point: 35°C; DSC onset: 165°C. ^{1}H NMR (d_6-dmso): 0.823, 0.825, 0.840, 0.844, 0.857 (multiplet, area 3.303); 1.236, 1.247, 1.258, 1.356, 1.378, 1.396 (multiplet, area 9.072); 4.320, 4.338, 4.355 (triplet, area 2.261); 7.012 (broad singlet, area 2.000), 9.175 (singlet, area 1.065), 10.230 (singlet, area 1.099). ^{13}C NMR (d_6-dmso): 13.918, 21.973, 25.327, 27.965, 28.034, 31.012, 51.784, 142.730, 145.298. Elemental analysis: %C: 44.07 (theory); 43.85 (found); %H: 7.80 (theory); 8.08 (found); %N: 28.55 (theory); 28.70 (found).

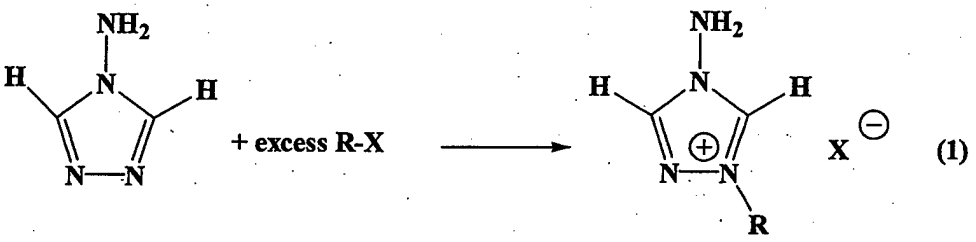
1-n-octyl-4-amino-1,2,4-triazolium nitrate (XXIV): In essentially the same manner as in **XIV** above, 1.0047 g., 3.62 mmoles, of 1-n-octyl-4-amino-1,2,4-triazolium bromide was reacted with silver nitrate, 0.6514 g., 3.83 mmoles, yielding 1-n-octyl-4-amino-1,2,4-triazolium nitrate, 0.9347 g., 3.60 mmoles, 99%. Melting point: 34°C; DSC onset: 165°C. ^{1}H NMR (d_6-dmso): 0.769, 0.826, 0.843, 0.855 (multiplet, area 3.049); 1.235 (broad singlet, 10.221); 1.823, 1.838 (multiplet, area 2.028); 4.312, 4.329, 4.346 (triplet, area 2.121); 7.000 (broad singlet, area 2.073), 1.806 (broad singlet); 9.184 (singlet, area 0.961), 10.218 (singlet, area 1.000). ^{13}C NMR (d_6-dmso): 13.988, 22.142, 25.442, 28.133, 28.365, 28.544, 31.230, 51.810, 142.845, 145.378. Elemental analysis: %C: 46.31(theory); 46.88 (found); %H: 8.16 (theory); 8.23 (found); %N: 27.00 (theory); 26.98 (found).

1-n-nonyl-4-amino-1,2,4-triazolium nitrate (XXV): As in **XIV** above, 1-n-nonyl-4-amino-1,2,4-triazolium bromide, 1.0039 g., 3.44 mmoles, was reacted with silver nitrate, 0.5855 g., 3.44 mmoles, , yielding 1-n-nonyl-4-amino-1,2,4-triazolium nitrate, 0.9339 g., 3.41 mmoles, 99%. Melting point: 53°C; DSC onset: 175°C. ^{1}H NMR (d_6-dmso): 0.834, 0.841, 0.851, 0.859, 0.867 (multiplet, area 3.119); 1.241(broad, area 12.725); 1.829, 1.845 (broad, area, 2.074); 4.300, 4.307, 4.318, 4.335 (multiplet, area 2.058); 6.944 (broad singlet, area 2.000); 9.179 (singlet, area 0.959), 10.172 (singlet, area 0.998). ^{13}C NMR (d_6-dmso): 13.950, 22.129, 25.419, 28.116, 28.385, 28.642, 28.813, 31.302, 51.789, 142.802, 145.322. Elemental analysis: %C: 48.33 (theory); 48.27 (found); %H: 8.48 (theory); 9.03 (found); %N: 25.61(theory); 25.44 (found).

1-n-decyl-4-amino-1,2,4-triazolium nitrate (XXVI): As in **XIV** above, 1-n-decyl-4-amino-1,2,4-triazolium bromide, 1.0085 g., 3.30 mmoles, was reacted with silver nitrate, 0.5606 g., 3.30 mmoles, resulting in 1-n-decyl-4-amino-1,2,4-triazolium nitrate, 0.8451 g., 2.94 mmoles, 84%. Melting point: 51°C; DSC onset: 185°C. ^{1}H NMR (d_6-dmso): 0.828, 0.844, 0.859 (triplet, area 4.021), 1.235 (broad singlet, area 15.760) 1.826, 1.841 (broad doublet, area 2.057), 4.310, 4.327, 4.344 (triplet, area 2.042); 6.993 (broad singlet, area 2.000), 9.178 (singlet, area 0.986), 10.209 (singlet, area 0.993). ^{13}C NMR (d_6-dmso): 13.948, 22.127, 25.409, 28.091, 28.365, 28.713, 28.849, 28.993, 31.317, 51.781, 142.774, 145.303. Elemental analysis: %C: 50.15 (theory); 50.26 (found); %H: 8.76 (theory); 9.40 (found); %N: 24.37 (theory); 24.48 (found).

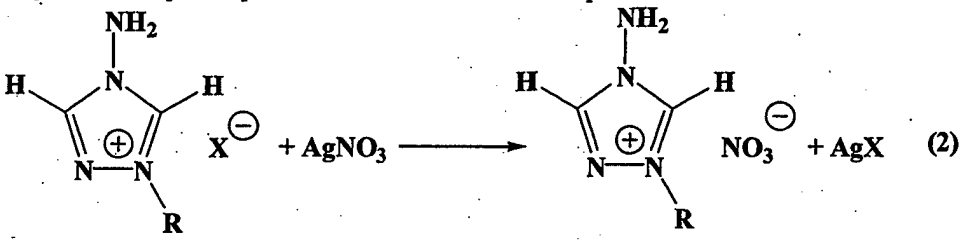
General synthesis and physical properties

Previously, a communication reported the synthesis of one substituted-1,2,4-triazoles in a one pot scheme via the alkylation of 4-amino-1,2,4-triazole forming 1-alkyl-4-amino-1,2,4-triazolium salts, with subsequent diazotization of the amino group, forming desired 1-substituted-1,2,4-triazoles[37]. However, the intermediates were not the focus as the real effort was directed towards the pharmaceutically active 1-substituted-1,2,4-triazoles.[44] Earlier efforts reported the alkylation of substituted 4-amino-1,2,4-triazoles, however, the efforts focused on 3, (5)-alkyl- and aryl- substituted 4-amino-1,2,4-triazoles[34-39]. Very recently a report was made on the synthesis of 1-substituted-4-amino-1,2,4-triazolium nitrates involving the amination of 1-substituted-1,2,4-triazoles with picryloxyamine followed by subsequent treatment with excess nitric acid forming new nitrate salts[40]. However this route is complicated with the use of the highly reactive picryloxyamine[45] and is not convenient for widespread use. It was realized that the intermediate 1-R-4-amino-1,2,4-triazolium halide salts have essentially the same overall shape as the well-known 1,3-dialkyl-imidazolium cation-based ionic liquids and might possess similar poor three-dimensional packing characteristics resulting in a new class of ionic liquids. Expanding and improving the reaction schemes previously reported[37], a large family of new 1-substituted-4-amino-1,2,4-triazolium salts have been synthesized and fully characterized. The synthesis of all of the materials was accomplished by the reaction of excess n-haloalkane (halo = Br, I) with 4-amino-1,2,4-triazole (> 2:1) typically in acetonitrile. The product salts precipitated from the reaction mixture upon cooling. (Reaction 1)



Use of less than a 2:1 mole ratio of alkyl halide to 4-amino-1,2,4-triazole led to extensive reaction times, incomplete conversion to alkylated product, as well as contamination of the ionic liquid product with 4-amino-1,2,4-triazole. Most of the materials precipitated as oils initially but could be induced to solidify by complete removal of the solvent, followed by recrystallization from hot acetonitrile or isopropyl alcohol. Densities were measured for all of the halides salts and are listed in Table 1. The materials follow the expected trend, as the alkyl chains length increases, the density drops in a gradual manner.

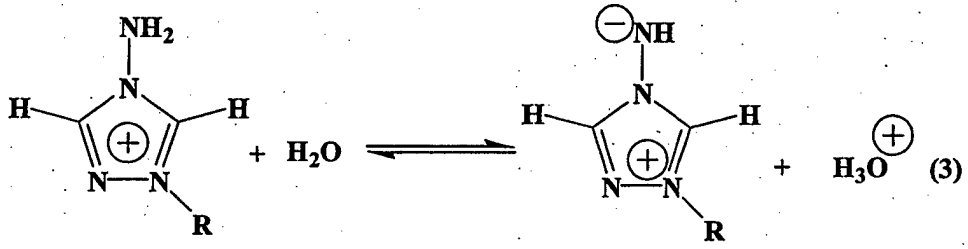
Subsequent metathesis of the 1-alkyl-substituted-4-amino-1,2,4-triazolium salts with silver nitrate in hot methanol, filtration of the unwanted silver halide salt, and subsequent removal of all the methanol from the ionic liquid product, resulted in high yields of high purity products. (Reaction 2). The ionic liquids could be recrystallized from hot ethyl acetate/methanol solutions which ridded the product of any silver salt contamination. In all cases the product salts were subsequently purified until no precipitate was observed from mixing a small aliquot of product salt with concentrated aqueous silver nitrate solution.



All of the ionic liquids were stable at room temperature and showed no signs of decomposition even after a year of storage at ambient temperatures. Melting points of the alkyl halide salts followed the expected increasing trend as the molecular weight increased. There were some anomalies most notable being the very high melting point of the 1-isopropyl-4-amino-1,2,4-triazolium bromide that is significantly higher than the corresponding n-propyl, n-butyl, or ethyl derivatives as can be seen in Table 1. Several of the nitrate salts had melt points at or below ambient temperatures, defining them as members of room temperature ionic liquids (RTILs) [2, 4]. While the melting point generally increased as the straight n-alkyl chain progressed from ethyl to n-decyl, one striking feature was that the salts with even numbered n-alkyl

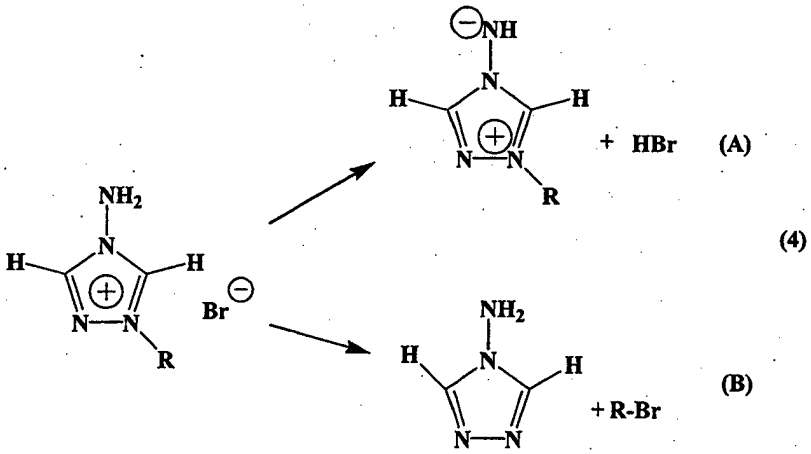
chains had lower melting points than those with odd numbered chains (see Table 2). There is no straight-forward answer for this trend as it is not observed in the corresponding halide salts or in similar imidazolium based salt systems. Nevertheless, all of the 1-substituted-1,2,4-triazolium halide and nitrate salts had melting points below 100°C defining them in the well known class of ionic liquids[3, 7].

All of the ionic liquids were soluble in water, methanol, ethanol, dimethylsulfoxide, dimethylformamide, hot acetonitrile and isopropanol, and were sparingly soluble in hot ethyl acetate, while insoluble in diethyl ether, tetrahydrofuran, and similarly low dielectric constant solvents. All of the materials were slightly hygroscopic, which complicated the collection of spectra. Another property unique to this family of compounds is the weakly acidic nature of all of the 1-R-4-amino-1,2,4-triazolium cations in aqueous solutions. Approximately 1M aqueous solutions of all the salts gave pHs in the range 3.5-4.5, strongly supporting the equilibrium of the 1-R-4-amino-1,2,4-triazolium cation with the 1-R-4-imino-1,2,4-triazoliuim zwitterion, giving K_a's for these alkylated heterocyclic cations ranging roughly from 3.0×10^{-5} to 3.0×10^{-4} (Reaction 3).



This is not surprising as the parent heterocycle 4-amino-1,2,4-triazole is weakly acidic[46-49], with aqueous solutions having a pH of around 5. Previous investigations with other substituted 4-amino-1,2,4-triazolium salts have found a wide array of reaction products stemming from this type of zwitterionic species including ring opening reactions in the presence of various bases[50, 51].

Ionic liquids have significant claims for their high temperature stability[1-5]. However, this stability depends not only on the cation but the nature of the corresponding anion. The size, charge delocalization and basicity of the parent heterocycle and anion weigh heavily in the overall stability of resultant salts. In the materials studied here the parent heterocycle, 4-amino-1,2,4-triazole, is a significantly poorer base by several orders of magnitude than 1-alkyl-imidazoles. Hence, it would be logical to expect the thermal stability of 1-alkyl-4-amino-1,2,4-triazolium halide salts to be less than that of the corresponding imidazolium analogues, and this is what is observed in differential scanning calorimetry studies. In Table 1, the melting point and decomposition onset, i.e. where the trace begins to have a positive slope and not the maximum of the exotherm, are listed for the halides, and the decomposition onsets are rather low. There are two different, plausible initial decomposition routes for the 1-alkylated-4-amino-1,2,4-triazolium halide salts; (A) Simple proton transfer from heterocyclic N-amino group to the bromide anion, forming a zwitterion and HBr; and (B) Re-alkylation of the bromide anion forming the starting materials (Reaction 4). However, the actual pathway of decomposition is unknown until further studies are carried out.



In the case of the nitrate salts, the melting points were typically lower than the halide salts, and the corresponding DSC decomposition onsets were considerably higher (Table 2). One plausible explanation for this difference is the charge delocalization over the nitrate anion versus the spherical bromide anion, as it is well documented that charge delocalized anions have significantly wider liquid ranges in imidazolium and triazolium based ionic liquid systems[1-5, 31-33, 52, 53].

Spectral properties of low melting salts

Several forms of spectroscopy were used to characterize the new salts including vibrational and multinuclear nmr spectra. ^{1}H and ^{13}C nmr revealed shifts in both the alkyl chains attached to the heterocyclic ring, as well as subsequent shifts in the heterocylic carbon and hydrogen signals. The 4-amino-1,2,4-triazole ring contains two C-H linkages in the ring as well as a pendant NH_2 group, which upon alkylation of the ring in the N(1) position, breaks the mirror symmetry of the ring. This is immediately evident in the proton spectra, with the disappearance of 4-amino-1,2,4-triazole's C-H singlet (+8.5 ppm), and the emergence of two, equal downfield C-H singlets (+9.2 ppm and +10.3 ppm). The NH_2 broad singlet has also been shifted to an average value of +7.1 ppm, a 0.7 ppm downfield shift from the neutral 4-amino-1,2,4-triazole. Also there was a 1 ppm downfield shift (average value +4.3 ppm) of the alkyl pendant group protons attached to the first carbon bonded to N(1) of the triazole ring, as compared to those of the alkyl halides. This was accompanied with subsequent smaller downfield shifts in the adjacent alkyl chain hydrogen environments. These shifts are most likely attributed to the + 1 formal charge placed upon the N(1) of 4-amino-1,2,4-triazole ring, as well as the alkyl chain being bonded to the electron withdrawing 4-amino-1,2,4-triazole ring. Such shifts are not unexpected or unreasonable and have been noted in simple protonated triazole systems[49, 54, 55], 1-R-4-amino-(3),(5)-substituted-1,2,4-triazolium salts[34-38], 1-R-4-nitramino-1,2,4-triazole zwitterions[41-43], as well as 1-4-difluoroalkylsubstituted-1,2,4-triazolium ionic liquids[31-33].

Similar effects were observed in the carbon 13 spectra; the loss of symmetry of the ring upon alkylation resulted in two singlets - one slightly upfield from the starting material and one shifted downfield from the 4-amino-1,2,4-triazole singlet. The shift can be explained by the carbon atom directly attached to the N(1) atom which has undergone alkylation, forcing more p character upon the C=N bond, resulting in an upfield shift, while the carbon atom on the far side of the ring experiences a loss of electron density in the ring but no real change in its direct bonding environment. The ^{13}C signals of the pendant alkyl group were shifted downfield with carbon attached directly to N(1) of the 4-amino-1,2,4-triazole ring having the largest shift, usually in the +50 to +55 ppm downfield which is typical of carbon nitrogen single bond environments, mirroring those shifts observed in the ^{1}H spectra and agree well with those reported in similar systems[30-33, 37, 40-42, 49, 56, 57].

The vibrational spectra are quite complex of all the new ionic liquids especially as alkyl chain lengths increase. N-H stretches are observable in both the infra-red and Raman ranging from 3400-3200 cm^{-1} as rather sharp bands and are not unusual[55]. The C-H bands of both the heterocyclic and alkyl chains are apparent but making absolute assignments of these bands is nearly impossible due to extensive hydrogen bonding. From the structure of parent heterocycle with an exocyclic N-amino group as well as information found in all the crystal structures to be discussed later, there was a tremendous amount of cation anion interactions between N-H and C-H protons of the heterocycle as well as with some of the C-H protons of the pendant alkyl groups. The vibrational spectra of all of the new salts are quite intense, complex, and broad in the region of 3350- 2600 cm^{-1} which is strong evidence of NH_2---X^- hydrogen bonding interactions and has been noted in many other amine systems[36-38, 58-67]. Bands typical of nitrate salts, 1375 cm^{-1} in the infrared and 1043 cm^{-1} in the Raman are easily observed in all the spectra and match well to those observed in other nitrate salt systems[68-70].

Single crystal x-ray diffraction studies of new salts

Several of the new salts were studied by single crystal x-ray diffraction studies at ambient and low temperatures and essentially gave the expected structures[71-74]. All of the materials were substituted at the N(1) of the 1,2,4-triazole ring with the alkyl group. Each of the new salts will be discussed on an individual basis. However there were no major trends that were noted among all of the crystal structures. In all the halide structures, the N-amino protons saddle the plane of the triazolium ring (above and below), sometimes with the lone pair facing towards the side of the ring N-alkylation (ethyl, isopropyl, n-propyl)

and away in the n-hexyl and n-heptyl bromide structures. It would have been thought that the lone pair of the N-amino group in the plane of the ring between atoms 3 and 4 of the 1,2,4-triazole ring would have a longer bond, but this was not the case. These structural features influence the corresponding bond lengths, as the ring C-N ring bond which faces the lone pair of N-amino group has a substantially longer bond than the ring C-N bond on the far side of the ring. Secondly, in all the structures there are significant interactions between the anions and the N-amino protons as well as the C-H protons of the heterocylic ring. Previously an x-ray diffraction study of the structure of 4-amino-1,2,4-triazole was reported[75], however we decided to reinvestigate the structure of the neutral heterocycle for a comparative study with the cationic structures.

4-amino-1,2,4-triazole crystallizes in a monoclinic cell with Cc symmetry and major details of the structural solution are shown in Table 3. The N-amino group in the 4 position of the ring has the NH_2 hydrogen atoms straddling the plane of the ring atoms in one direction. There are two asymmetric heterocyclic rings in the unit cell (Figure 1). The bond distances within the ring structure follow the trends that would be expected for the neutral 4-amino-1,2,4-triazole where the two formal double bonds of the triazole ring are between N(1) and C(5) and N(2) and C(3). The other bonds within the 1,2,4-triazole ring have distances that are slightly longer than these, however all bonds are shorter than typical C-N and N-N single bond distances[76], supporting the idea of ring delocalization of pi bond electrons.

Hydrogen bonding is very pronounced in the structure with several significant contacts, which are within Van der Waal distances[77](Figure 2). The most significant are the N-amino hydrogen contacts to nitrogen atoms either N(1) or N(2) of the neighboring 4-amino-1,2,4-triazole ring. However, despite these contacts there are no significant variances in any of the bond distances in either asymmetric ring in the unit cell, within experimental error.

1-ethyl-4-amino-1,2,4-triazolium bromide (**II**) crystallized as a monoclinic crystal system with $P2_{(1)}/n$ space group symmetry, and the crystal structure is shown in Figure 4 with details of the x-ray study summarized in Table 3. Several of the bond distances in the heterocyclic ring of the 1-ethyl-4-amino-1,2,4-triazolium cation have been affected due to the alkylation of the triazole ring. With alkylation of the ring there is a formal +1 charge placed upon the site of alkylation, the N(1) atom of the 1,2,4-triazole ring, and it would be expected that the bonds to N(1) of the 1,2,4-triazole ring would be affected. In the alkylated heterocyclic ring, the C(2)-N(1) bond distance of 1.312(2) Å and the C(1)-N(2) bond distance of 1.310(2) Å are essentially the same and reflect the expected sp^2 C=N bond distances. The N-amino N(1)–N(2) distance of 1.369(2) Å is slightly shorter than that observed in the neutral 4-amino-1,2,4-triazole structure and is slightly shorter than a typical N-N single bond distance (1.40 Å)[75, 78-85]. The heterocyclic C-H bond distance of C(1)–H(1) is 0.99(3) Å is slightly longer than the C(2)-H(2) distance of 0.94(3) Å. The C(2) atom is bonded directly to the quarternarized N(1) of the ring which could explain the shortness of the the C(2)-H(2) bond through inductive effects. However, these C-H bond distance differences are also significantly affected by strong interactions with the bromide anions. The other major bonds of the ring C(1)-N(3) and C(2)-N(3) at 1.356(3) Å and 1.337(2) Å , respectively, vary somewhat from that observed in the neutral material. Surprisingly, the C(2)-N(3) bond is shorter despite its proximity to the N-amino lone pair which saddles the ring on the same side of the ring, while the C(1)-N(3) bond is longer despite being in vicinity of the N-amino protons. This suggests that quarternization of the neighboring nitrogen in the triazole ring plays a more important role inductively shortening the C-N bond nearest it. The N(3)-N(4) bond distance, 1.419(2) Å, is very similar to that in the neutral material. Otherwise the C-H and N-H bond distances of the heterocyclic ring are significantly different N(4)-H(3) = 0.92(2) Å while N(4)-H(4) = 0.83(2) Å is shorter which can probably be attributed to hydrogen bonding to the bromide anion. The bond distances in the alkyl chain do not vary tremendously and the corresponding angles between all of the atoms of the heterocyclic cation are within the expected values and will not be discussed.

Hydrogen bonding in ionic liquids has been a significant point of interest amongst several researchers with most of the discussion based on interactions of various substituted imidazolium chloride salts[86-90]. Another report has discussed significant interactions between 1-ethyl-3-methyl imidazolium cation and its iodide counterion[91]. The only other example of a structurally characterized ionic liquid containing bromine atoms is that of the 1-ethyl-3-methylimidazolium tri-u-bromo-bis[tribromoruthenate(III)][92] where the authors saw no significant cation-anion interactions. In Figure 4, all of the significant interactions between the cations and anion are shown by dotted lines. Also evident is the effect on the corresponding bond length of the bonded hydrogen atom. Several of the hydrogen bromide interactions are much less than the sum of the Van der Waal radii (3.3 Å)[77], The shortest contact of 2.53(2) Å between the anion and cation, Br(1) – H(3), of the N-amino group (with a Br-H-N angle of 164.1(2)°) accords to the longer N-amino N-H bond distance 0.92(2) Å and is the strongest interaction of the structure.

All of the cation anion interactions are listed in Figure 4. As expected, the strong bromide hydrogen interactions lead to lengthening of the associated N-H or C-H single bond distances.

1-n-propyl-4-amino-1,2,4-triazolium bromide (**III**) crystallized in a triclinic cell with P-1 symmetry with two asymmetric 1-n-propyl-4-amino-1,2,4-triazolium cations as well as two corresponding bromide anions. A view of the crystal structure is in Figure 5, with the details of the x-ray study in Table 3. Bond distances in the cation have not been significantly affected by the alkylation of the ring. In both cations, the nitrogen- nitrogen bond distance in the two heterocyclic rings (N(1)-N(2) = 1.372(3) Å and N(5)-N(6) = 1.374(3) Å) are nearly identical and are essentially unchanged to those found in the parent heterocyle. The carbon nitrogen bond distances in the 1,2,4 triazolium rings corresponding to C(2)-N(1) and C(1)-N(1) are fairly short and typical of carbon nitrogen double bonds[76, 93-100]. The C-N bond distances corresponding to C(1) and C(2) bonded to N(4) of the parent 1,2,4-triazole ring are all significantly shorter than typical C-N single bonds yet are longer than typical C=N bond lengths and are typical to those observed in triazole systems[78-85, 93-100]. The C-N bonds which are closer to the alkylated N(1) position of the 1,2,4-triazole ring are slightly shorter (C(2)-N(3) = 1.329(3) Å and C(7)-N(7) = 1.328(3) Å) than the corresponding C-N bond distances on the far side of the ring [C(1)-N(3) = 1.364(4) Å and C(6)-N(7) = 1.365(3) Å] and could be interpreted as a result of the alkylation and quarternization of the N(1) position of the 1,2,4-triazole ring, similar to what was observed in the 1-ethyl-4-amino-1,2,4-triazolium bromide above. The N-NH_2 bond lengths in both triazolium cations are essentially the same (N(3)-N(4) = 1.414(3) Å and N(7)-N-(8) = 1.418(3) Å) and vary little from the starting heterocycle.

There is a large amount of hydrogen bonding present in the unit cell between both asymmetric bromide anions and the corresponding cations that is within Van der Waal distances (3.03 A)[77] and is depicted in Figure 6. Symmetry related cations have been placed in the view to illustrate all of the asymmetric hydrogen bromide contacts that are shorter than the sum of the Van der Wall radii. The most significant contacts are between the N-amino hydrogen atoms and the bromide anions in the structure. There is also a significant effect on the N-amino hydrogen bond distances with the N(4)-H(4) bond distance of 0.79(3) Å, being significantly shorter than the N(4)-H(3) bond distance (0.87(3) Å)in the first 1-n-propyl-4-amino-1,2,4-triazolium cation. However in cation 2, both the N(8)-H(14) and N(8)-H(15) bond distances are 0.84(3) Å despite hydrogen bonding. There is no obvious reason for this bond variance present in one ring despite the fact that all the N-amino hydrogen atoms are involved in significant interactions with the bromide anions.

1-isopropyl-4-amino-1,2,4-triazolium bromide(**IV**) crystallized in a triclinic cell with P-1 symmetry. There is one asymmetric cation and anion in the unit cell (Figure 7). The bond lengths and angles are typical as in the previous examples. The N(1)-C(2) and N(2)-C(1) bond lengths are nearly the same at 1.298(3) Å and 1.297(3) Å, which show significant C=N double bond character. The other two carbon nitrogen bonds (C(1)-N(3), distance 1.355(3) Å, and C(2)-N(3), distance 1.327(3) Å) follow the same trend as observed in the other salt structures with the C-N bond that is closer to the site of N-alkylation being the shorter bond. Once again the C-N bond lengths are between that of a typical single bond and that of a double bond, indicating charge delocalization. The N(3)-N(4) bond length is 1.400(3) Å and is essentially identical to all those in the other cation structures of this study. The bonds in the isopropyl group are all within typical C-C, C-N, and C-H bond distances as well[76].

There is a large amount of hydrogen bond contacts with the sum of the Van der Wall radii (3.03 Å)[77] in the crystal lattice and they are depicted in Figure 8, revealing a complex three dimensional structure. As in the previous structures there is a difference between the N-amino hydrogen bond distances but it is not as prominent (N(4)-H(3) = 0.86(3) Å, and N(4)-H(4) = 0.92(4) Å) since both hydrogen atoms are involved in significant interactions with the bromide counterion.

1-n-hexyl-4-amino-1,2,4-triazolium bromide (**VIII**) crystallized as thin plates in a monoclinic cell with P21/c symmetry. There was one asymmetric cation and anion in the unit cell (Figure 9). The bond distances are mostly similar to the above mentioned structures but there are some significant differences. The pendant n-alkyl chain has assumed the common low energy "zig-zag" chain radiating away from the triazole ring. Once again the N-amino group is in a saddle position with the primary plane of the triazole ring, however in this structure, the N-amino group hydrogen atoms are facing the side where alkylation of the heterocyclic ring nitrogen has taken place, instead of facing away as in the proceeding structures. The bond distances follow the trend observed in the previous cation structures, where the C-N bond distance closest to the site of N(1) alkylation (C(2)-N(3) = 1.334(4) Å) is shorter than that of the C-N bond distance on the opposite side of the ring (C(1)-N(3) = 1.350(4) Å), but the difference between the bond lengths is not as pronounced as in the cations with shorter alkyl side chains.

Hydrogen bonding contacts are most prominent between the N-amino hydrogen atoms and the bromide anion as well as in a few interactions between the hydrogen atoms attached to the carbon atoms of the 1,2,4-triazole ring shown in Figure 10. The N-amino hydrogen bond distances are asymmetric with an N(4)-H(4C) distance of 0.93(3) Å and an N(4)-H(4D) distance of 0.81(3) Å, following the general trend noted in all the heterocyclic salts in this paper. With the much longer alkyl side chain, the structures are exhibiting hydrophobic/hydrophilic packing tendencies. There is an orthogonal arrangement of the cations with the n-hexyl side chain that radiates away from the triazolium ring to start forming a "head to tail" arrangement of the cations with the accompanying bromide anions. Thus, pockets are formed between the N-amino groups of the 4-amino-1,2,4-triazole cationic rings. In the packing diagram shown in Figure 10, this is much more apparent. This compares as well as contrasts with one dimensional layered behavior noted in long n-alkyl substituted imidazolium salt systems which display liquid crystalline behavior[101-103].

1-n-heptyl-4-amino-1,2,4-triazolium bromide (**IX**) crystallized in a monoclinic cell with P21/c symmetry and is shown in Figure 11. The structure is very similar to the n-hexyl-4-amino-1,2,4-triazolium bromide salt reported above with one asymmetric cation and anion per unit cell. Once again the n-heptyl alkyl chain radiates away from the triazolium ring in the "zig-zag" structure. The N-amino group saddles the ring, and as in the n-hexyl salt, the N-amino-group hydrogen atoms are pointed towards the alkylated N(1) position of the triazole ring. The bond distances in the ring follow the trend of all the triazolium cations and are very similar in bond distances. The bonds between carbon nitrogen atoms of the heterocyclic ring (N(1)-C(2) = 1.314(4) Å and N(2)-C(1) = 1.303(4) Å) are essentially the same and their distances denote double bond character as would be expected. The other carbon nitrogen bonds (C(1)-N(3) = 1.357(4) Å and C(2)-N(3) = 1.333(3) Å), follow the trend where the shorter of the bonds, C(2)-N(3), is nearer to the point of N-alkylaton of the ring, closest to the quarternized nitrogen, N(1). However, it appears that with the N-amino hydrogen atoms facing this bond, there is not as great a difference between the carbon-nitrogen bond distances,(C(1)-N(3) and C(2)-N(3)) as those observed in the smaller alkyl side chained cations reported above. This mirrors the behavior observed in 1-n-hexyl-4-amino-1,2,4-triazolium bromide (**VIII**). Otherwise the bond distances are not out of the ordinary and match well to those observed in other heterocyclic systems[78-85, 93-100] and will not be discussed further.

As in the n-hexyl substituted cation, hydrogen bonding appears to strongly influence the overall packing of 1-n-heptyl-4-amino-1,2,4-triazolium bromide. The strongest interactions are between the N-amino hydrogen atoms and the bromide which leads to the formation of a two-dimensional structure of n-heptyl chains lining up, end to end, with the triazolium rings forming pockets for the bromide anions (illustrated in Figure 12). The packing structure is essentially identical to that illustrated for the 1-n-hexyl-4-amino-1,2,4-triazolium bromide in Figure 10 above. The bond distances for the N-amino hydrogen bonds are significantly affected with the N(4)-H(4C) distance of 0.90(4) Å, while the N(4)-H(4O) distance of 0.80(5) Å is considerably shorter. Previously, Seddon et al.[101-103] have described liquid crystal behavior with longer chained n-alkyl methylimidazolium salts exhibiting smectic properties. The longer n-alkyl-4-amino-1,2,4-triazolium based salts appear to have the same kind of physical properties, but this will have to be validated with further work that is outside the scope of this study.

Two crystal structures were obtained for the corresponding family of nitrate salts which generally were much more difficult to crystallize than their halide analogues. 1-isopropyl-4-amino-1,2,4-triazolium nitrate (**XVIII**) crystallized in a triclinic cell of P-1 symmetry with a view of the structure in Figure 13. There is one asymmetric cation and one nitrate anion in the structure. One important difference in the structure of the nitrate salts versus the halide salts is the relative position of the N-amino group in relation to the triazole ring. In the 1-isopropyl-4-amino-1,2,4-triazolium nitrate structure, the cation has a twisted N-amino group which doesn't saddle the triazole ring in a symmetric fashion as observed in the halide structures. The C(1)- N(4) bond distance, 1.316(3) Å, and C(2)-N(5) bond distance, 1.305(4) Å are very similar to that observed in all the structures within this study as well as several others elsewhere, revealing significant double bond character[78-85, 93-100]. The C(1)-N(3) bond distance (1.338(3) Å) is nearest to the site of N-alkylation, is shorter than the other C-N bond (C(2)-N(3) = 1.354(3) Å) and agrees well with the trend observed here as well as in other systems where the C-N bond closest to the site of alkylation is shorter than the corresponding bond on the far side of the ring. In direct contrast, the N-amino hydrogen bond distances are essentially the same (N(2)-H(3) = 0.90(3) Å and N(2)-H(4) = 0.92(4) Å) which is somewhat surprising despite the significant amount of hydrogen bonding. All of the carbon nitrogen bond distances are within typical bond distances in comparison with other similar triazole based materials, 3,4,5-triamino-1,2,4-triazolium bromide[82] as well as 1,2,4-triazolium perchlorate[55] and several 1-N-coordinated 4-amino-

1,2,4-triazole based salts[83-85]. The nitrate anion is planar and its angles and bond distances are typical for those observed in nitrate salts[104-107] and they will not be discussed.

Hydrogen bonding is very pronounced in 1-isopropyl-4-amino-1,2,4-triazolium nitrate with extensive hydrogen atom contacts between the oxygen atoms of the nitrate anion and many of the hydrogen atoms present in the cation (Figure 14). However there appears to be no major perturbation in any of the bond distances despite these rather significant contacts. Extensive hydrogen bonding probably explains the "twist" of the N-amino group out of the saddle position of the triazole ring since several of the N-amino proton contacts are very short (N(2)-H(3)---O(3) = 2.11(3) Å, N(2)-H(4)---O(1) = 2.08(4) Å) and are much shorter than that of the sum of Van der Waal radii 2.72 Å[77]. Additionally there are many contacts between the nitrate anion oxygen atoms and both the heterocyclic carbon hydrogen atoms and several of the isopropyl carbon hydrogen atoms. However, many of these carbon hydrogen bond distances have been fixed in the structure refinement process and this must be considered in the arguments.

1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate (XX) crystallized in a monoclinic cell with P21/n symmetry and is shown in Figure 15. There is one asymmetric cation and an accompanying nitrate anion in the unit cell. As in the 1-isopropyl-4-amino-1,2,4-triazolium nitrate structure, the N-amino group is "twisted" out of the saddle position with the plane of the 1,2,4-triazole ring. This, again, is most likely due to the extensive hydrogen bonding within the crystal structure. The distances in the heterocyclic ring are all within normal bonding distances there is not a lot of variance between the C-N bonding environments in the heterocyclic ring as noticed in all of the other structures. The carbon nitrogen bond distance closest to the site of N-alkylation, C(1)-N(4) = 1.3104(17) Å, while the corresponding C-N bond distance on the far side of the ring, C(2)-N(3) = 1.3027(18) Å, are essentially the same which follows the common trend seen in 1,2,4-triazole systems[78-85, 93-100]. As well the other C-N bond distances in the ring follow the trend where the C-N closest to the site of alkylation (C(1)-N(1) =1.3317(17) Å) is the shorter than the other C-N bond (C(2)-N(1) = 1.3543(17) Å). As was observed in 1-isopropyl-4-amino-1,2,4-triazolium nitrate (XVIII), the N-amino hydrogen bond distances are essentially the same (N(2)-H(2A) = 0.894(17) Å and N(2)-H(2B) = 0.884(17) Å) despite significant hydrogen bonding to the nitrate anion. As in the preceding nitrate structure, the nitrate anion is planar and its bond distances and angles are typical to those that have been observed in other nitrate salts[104-107] and they will not be discussed further.

Hydrogen bonding is rather significant in 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate with many contacts between the oxygen atoms of the nitrate anion and hydrogen atoms of the N-amino group, the carbon hydrogen atoms of the heterocyclic ring as well as some contacts with the hydrogen atoms of the pendant methylcyclopropyl ring (Figure 16). Many of these are well within Van der Waal bonding distances[77] and are listed in Figure 16 caption. Nevertheless, despite this large amount of hydrogen bonding, all of the bond distances in the structure are not drastically affected from normal distances observed in other structures, and it seems to be a structure which illustrates large coulombic interactions between the cation and anion.

Conclusions

A large new family of ionic liquids based upon 1-substituted-4-amino-1,2,4-triazolium cations with halides and nitrate anions have been synthesized and well characterized. These new ionic liquids display typical ionic liquid behaviors akin to their dialkyl-imidazolium relatives, such as low melting points and long liquidous ranges, however differ with their weak acidity, lessened thermal stability and high solubility in polar solvents. X-ray diffraction studies of several of the new salts revealed the expected structures with 1-substituted-4-amino-1,2,4-triazolium cations with bromide and nitrate anions. Extensive hydrogen bonding was very prevalent between the N-amino group protons and the corresponding anions, however bond distances in the cation were not dramatically affected in any significant manner. As well the longer alkyl chained 1-R-4-amino-1,2,4-triazolium halide salts had unusual packing properties which warrants further investigations.

Acknowledgements

The authors would like to thank Dr. Michael Berman (AFOSR) and Mr. Michael Huggins (AFRL/PRS), Mr. Ronald Channel and Mr. Wayne Kalliomaa (AFRL/PRSP) for funding and encouragement of this research effort. As well the authors are grateful to Bret Wight for carrying out some

of the elemental analyses. One author (GWD) is grateful to stimulating discussions and support from Jeff Bottaro and Mark Petrie (SRI International, Inc.) as well as Jeffrey Sheehy (NASA Marshall SFC).

References Cited

1. Holbrey, J.D.; Seddon, K.R. *Clean Products and Processes.* **1999,** 1, 223-236.
2. Welton, Thomas. *Chem. Rev.* **1999,** 99, 2071-2083.
3. Wasserscheid, Peter; Keim, Wilhelm. *Agnew Chem. Int. Ed.* **2000,** 39, 3772-3789.
4. Seddon, K. R. *Kinetics and Catalysis* **1996,** 37, 693-696.
5. Wassershceid, P. ; Welton, T. (eds) Ionic Liquids in Synthesis Wiley-VCH **2003,** Fed. Rep. Germ.
6. Rogers, R.; Seddon, K. (eds.) Ionic LiquidsIndustrial Applications for Green Chemistry ACS Symposium Series 818, American Chemical Society, Wash., D.C., **2002.**
7. Hagiwara, Rika; Ito, Yasuhiko *J. Fluor. Chem.* **2000,** 105, 221-227.
8. Wilkes, John S. *Green Chemistry.* **2002,** 4, 3-10.
9. Wilkes, John S.; Zaworotko, Michael J. *J. Chem. Soc. Chem. Commun.* **1992,** 965-96.
10. Fuller, Joan; Carlin, Richard T.; De Long, Hugh C.; Haworth, Dustin *J. Chem. Soc. Chem. Commun.* **1994,** 299-300.
11: Sherif et al. U.S. Patent 5,731,101, **1998.**
12. Huddleston, Jonathon; Willauer, Heather; Swatloski, Richard; Visser, Ann; Rogers, R. *Chem. Commun.* **1998,** 1765-1766.
13. Green, Laine; Homeon, Ivan; Singer, Robert D. *Tetrahedron Letters.* **2000,** 41, 1343-1346.
14. Abdul-Sada et al. U.S. Patent 5,994,602 **1999.**
15. Chauvin, Yves; Mussmann, Lothar; Olivier, Hélène. *Agnew. Chem. Int. Ed. Engl.* **1995,** 34, 2698-2700.
16. Hussey, Charles L. *Pure & Appl. Chem.* **1988,** 60, 1763-1772.
17. Sherif, Fawzy, G. et al. U.S. Patent 5,731,101 **1998.**
18. Dyson, Paul; Grossel, Martin; Srinivasan, Narmatha; Vine, Tracey; Welton, Thomas; Williams, David; White, Andrew; Zigras, Theodore J. Chem. Soc. Dalton Trans. **1997,** 3465-3469.
19. Koecher, Juergen et al. U.S. Patent 5,128,267 **1992.**
20. Munson et al. U.S. Patent 6,339,182 **2002.**
21. Koch et al. U.S. Patent 5,827,602 **1998.**
22. Teles et al. U.S. Patent 5,508,422 **1996.**
23. Schneider et al. U.S. Patent 5,840,894 **1998.**
24. Ambler, Philip et al. U.S. Patent 5,304,615 **1994.**
25. Gordon, Charles *Applied Catalysis A. General* **2001,** 222, 101-117.
26. Suarez, Paulo; Dullius, Jeanne; Einloft, Sandra; DeSouza, Roberto; Dupont, J. *Polyhedron* **1996,** 15, 1217-1219.
27. Davis, James; Forrester, Kerri *Tetrahedron Letters* **1999,** 40, 1621-1622.
28. Curphey, T. J.; Prasad, K. S. *J. Org. Chem.* **1972,** 37, 2259-2265.
29. Vestergaard, B,; Bjerrum, N.J.; Petrushina, I.; Hjuler, H.A.; Berg, R.W.; Begtrup,M. *J. Electrochem. Soc.* **1993,** 140, 11, 3108-3113.
30. Surpateanu, Gheorghe; Lablanche-Combier, Alain; Grandglaudon, Pierre; Couture, Alain; Mouchel, B. *Revue Roumaine de Chemie.* **1993,** 38, 6, 671-681.
31. Mirzaei, Yousef R.; Twamely, Brendan; Shreeve, Jean'ne M. *J. Org. Chem.* **2002,** 67, 9340-9345.
32. Singh, R. P.; Manandhar, S.; Shreeve, J. M. *Tetrahedron Letters*, **2002,** 43, 9497-9499.
33. Mirzaei, Y.; Shreeve, J. M. *Synthesis*, **2003,** 24-26.
34. Becker, Von Heinz G.O.; Böttcher, Horst; Röthling, Thilo; Timpe, Hans-Joachim. *Wissenschaftl. Zeitscher.* **1966,** 8, Heft 1, 22-25.
35. Becker, H.; Timpe, H. *J. Prakt. Chem.* **1969,** 311, 9-14.
36. Becker, H.; Nagel, D.; Timper, H. *J. Prakt. Chem.* **1973,** 315, 1131-1138.
37. Astleford, Bret A.; Goe, Gerald L.; Keay, James G.; Scriven, Eric F. *J. Org. Chem.* **1989,** 54, 731-732.
38. Gromova, S.A.; Barmin, M.I.; Shylapochnikov, V. A..; Kolesnikova, O. A.; Mel'nikov, V.V. *Russian Journal of Organic Chemistry.* **1996,** 32, 8, 1190-1193.
39. Gromova, S.A.; Barmin, M.I.; Mel'nikov, A.A.; Korolev, E.A.; Mel'nikov, V.V. *Russian Journal of Applied Chemistry.* 72, 8, 1409-1411.

40. Shitov, O.P.; Vyazkov, V.A.; Tartakovskii, V.A. *Izv. Akad. SSSR, Ser. Khim.* **1989**, 11, 2654.
41. Shitov, O.P.; Korolev, V.L.; Tartakovsky, V.A. *Russ. Chem. Bull.* **2002**, 51, 3, 499-502.
42. Shitov, O.P.; Korolev, V.L.; Bogdanvo, V.S.; Tartakovsky, V.A. *Russ. Chem. Bull.* **2003**, 52, 3, 695-699.
43. Kofman, T.P.; Kartseva, G.Yu.; Shcherbinin, M.B. *Russ. J. Org. Chem.* **2002**, 38, 9, 1343-1350.
44. Balasubramanian, Marudai; Keay, James G.; Scriven, Eric F.V. *Heterocycles.* **1994**, 37,3, 1951-1975.
45. Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis.* **1977**, 1-17.
46. Milicent, René; Redeuilh, Catherine. *J. Heterocyclic Chem.* **1980**, 17, 1691-1696.
47. Barszcz, Barbara; Gabryszewski, Mieczyslaw; Kulig, Jacek; Lenarcik, Beniamin. *J. Chem. Soc. Dalton Trans.* **1986**, 2025-2028.
48. De la Concepción Foces-Foces, M.; Cano Hernandez, Félix; Claramunt, Rosa M.; Sanz, Dionísia; Catalán, Javier; Fabero, Fernando; Fruchier, Alain; Elguero, José. *J. Chem. Soc. Perkin Trans 2.* **1990**, 237-244.
49. Claramunt, Rosa M.; Sanz, Dionísia; Catalán, Javier; Fabero, Fernando; Garcia, Norman; Foces-Foces, Concepción; llamas-Saiz, Antonio L.; Elguero, José. *J. Chem. Soc. Perkin Trans 2.* **1993**, 1687-1699.
50. Temple, C.; Montgomery, J. The Chemistry of Heterocyclic Compounds; Triazoles 1,2,4 **1981** J. Wiley & Sons, NY, NY, 599-658.
51. Becker, Von Heinz G.O.; Nagel, D.; Timpe, H. J. *J. Prakt. Chem.* **1973**, Band 315, 97-105.
52. Bonhôte, Pierre; Dias, Ana-Paula; Papageorgiou, Nicholas; Kalyanasundaram, Kuppuswamy; Grätzel, Michael. *Inorg. Chem.* **1996**, 35, 1168-1178.
53. Larsen, Anna S.; Holbrey,John D.; Tham, Fook S.; Reed, Christopher A. *J. Am. Chem. Soc.* **2000**, A-I.
54. Barlin, G.B.; Batterham, T.J. *J. Chem. Soc.(B).* **1967**, 516-518.
55. Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M.; Vij, A.; Ismail, I. *Prop. Expl. Pyrotech.* **2003**, 28, 174-180.
56. Weigert, Frank J.; Roberts, John D. *JACS.* **1968**, 90, 13, 3543-3549.
57. Wofford, D.S.; Forkey, D.M.; Russell, J.G. *J. Org. Chem.* **1982**, 47, 5132-5137.
58. Lieber, Eugene; Levering, Dewey Robert; Patterson, Lorna J. *Anal. Chem..* **1951**, 23, 11, 1594-1604.
59. Biles, F.; Endredi, H.; Keresztury, G. *J. Mol. Struct.* **2000**, 530, 183-200.
60. Edsall, John T.; Scheinberg, Herbert. *J. Chem. Phys.* **1940**, 8, 520-525.
61. Bellanato, Juana. *Spectrochimica Acta.* **1960**, 16, 1344-1357.
62. Chenon, Bernadette; Sandorfy, C. *Can. J. Chem.* **1958**, 36, 1181-1206.
63. Durig, J.R.; Bush, S.F.; Mercer, E.E. *J. Chem. Phys.* **1966**, 44, 11, 4238-4247.
64. Edsall, John T. *J. Chem. Phys.* **1937**, 5, 225-237.
65. Catalano, Edward; Sanborn, Russell H.; Frazer, Jack W. *J. Chem. Phys.* **1963**, 38, 9, 2265-2272.
66. Steiner, Thomas. *Agnew. Chem. Int. Ed.* **2002**, 41, 48-76.
67. Decius, J.C.; Pearson, D.P. *JACS.* **1953**, 75, 2436-2349.
68. Nakagawa, I.; Walter, J.L. *J. Chem. Phys.* **1969**, 51, 4, 1389-1397.
69. Rousseau, D.L.; Miller, R.E. *J. Chem. Phys.* **1968**, 48, 8, 3409-3413.
70. Walrafen, G. E.; Irish, D.E. *J. Phys. Chem.* 1964, 911-913.
71. X-ray Crystallography. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74° and using $MoK_{\square}$ radiation ($\square$ = 0.71073 Å) from a fine-focus tube. This diffractometer was equipped with KryoFlex apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop with a magnetic base, was then used to mount the crystals using PFPE (perfluoropolyether) oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of ten-second per frame at a detector resolution of 512 x 512 pixels using the SMART software.[1] A total of 1271 frames were collected in three sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running on Windows NT software by using the SAINT software[2] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS[3] program. The structures were solved by the direct method using the SHELX-90[4] program and refined by the least squares method on F^2, SHELXL-97[5] incorporated in SHELXTL Suite 5.10 for Windows NT.[6] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located either from difference electron density maps or generated at

calculated positions . 1. SMART V 4.045 Software for the CCD Detector System, Bruker AXS, Madison, WI (1999). 2. SAINT V 4.035 Software for the CCD Detector System, Bruker AXS, Madison, WI (1999). 3. SADABS, Program for absorption correction for area detectors, Version 2.01, Bruker AXS, Madison, WI (2000). 4. Sheldrick, G. M. SHELXS-90, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1990. 5. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997. 6. SHELXTL 5.10 for Windows NT, Program library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI (2000).
72. SMART for WNT/2000, version 5.625 **2001**, Bruker AXS, Inc., Madison, WI.
73. SAINT PLUS, version 6.22 **2001**, Bruker AXS, Inc., Madison, WI.
74. SHELXTL, version 6.10 **2000**, Bruker AXS, Inc., Madison, WI.
75. Starova, G. L.; Frank-Kameneckaya, O.V.; Levner, M.S. *Vestn. Leningr. U., Fiz. Khim.* **1991**, 103.
76. Conquest V. 1.5, Cambridge Structural Database System Version 5.24 (July Update, 2003) CCDC, Cambridge, UK, **2003**.
77. Bondi A. *J. Phys. Chem.* **1964**, 68, 441-451.
78. Drabent, K.; Ciunik *Chem. Commun.* **2001**, 1254.
79. Isaacs, N. W.; Kennard, C. H. L. *J. Chem. Soc. (B)* **1971**, 1270-1273.
80. Seccombe, R. C.; Kennard, C. H. L. *J. Chem. Soc. Perkin Trans. II* **1973**, 9-11.
81. Seccombe, R.C.; Tillack, J.V.; Kennard, C.H.L. *J.C.S. Perkin II.* **1973**, 6-8.
82. Seccombe, R.C.; Kennard, C.H.L. *J.C.S. Perkin II.* **1972**, 1-3.
83. Podberezskaya, N.V.; Pervukhina, N.V.; Doronin, V.P. *Zhurnal Strukturnoi Khimii.* **1991**, 32, 34-39.
84. Liu, Jia-Cheng; Fu, De-Gang; Zhuang, Jin-Zhong; Duan, Chun-Ying; You, Xiao-Zeng. *J. Chem. Soc, Dalton Trans.* **1999**, 2337-2342.
85. Drabent, K.; Ciunik, Z. *Chem. Commun.* **2001**, 1254-1255.
86. Wilkes, J.S.; Levisky, J.A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, 21, 1263-1264.
87. Tait, Stephen; Osteryoung, R. A. *Inorg. Chem.* **1984**, 23, 4252-4360.
88. Fannin, A.; King, L.; Levisky, J.; Wilkes, J. *J. Phys. Chem.* **1984**, 88, 2609-2614.
89. Wilkes, John S.; Hussey, Charles L.; Sanders, John R. *Polyhedron.* **1986**, 5, 1567-1571.
90. Dymek, C.; Stewart, J. *Inorg. Chem.* **1989**, 28, 1472-1476.
91. Abdul-Sada, A.; Greenway, A.; Hitchcock, P.; Mohammed, T.; Seddon, K.; Zora, J. *J. Chem. Soc. Chem. Commun.* **1986**, 1753-1754.
92. Appleby, D.; Hitchcock, P. ; Seddon, K.; Turp, J.; Zora, J.; Hussey, C.; Sanders, J.; Ryan, T. *J. Chem. Soc. Dalton Trans.* **1990**, 1879-1887.
93. Gorter, S.; Engelfriet, D. Acta *Crystallogr., Sect. B. Struct. Crystallogr. Cryst. Chem.* **1981**, 37, 1214.
94. Haasnoot, J.; De Keyzer, G.C.M.; Verschoor, G.C. *Acta Crystallogr., Sect. C:Cryst. Struct. Commun.* **1983**, 39, 1207.
95. Driessen, W.; De Graaff, R.; Vos, J. *Acta Crystallogr., Sect. C:Cryst. Struct. Commun.* **1983**, 39, 1635.
96. Lynch, D.; Smith, G.; Byriel, K.; Kennard, C. *Acta Crystallogr., Sect. C:Cryst. Struct. Commun.* **1994**, 50, 1291.
97. Engelfriet, D.; Groeneveld, W. ; Nap, G. *Z. Naturforsch., Teil A* **1980**, 35, 1387.
98. Lynch, D.; Latif, T.; Smith, G.; Byriel, K.; Kennard, C.; Parsons, S. *Aust. J. Chem.* **1998**, 51, 403.
99. Lynch, D.; Dougall, T.; Smith, G.; Byriel, K.; Kennard, C. *J. Chem. Cryst.* **1999**, 29, 67.
100. Goldstein, P.; Ladell, J.; Abowitz, G. *Crystallogr., Sect. B. Struct. Crystallogr. Cryst. Chem.* **1969**, 25, 135.
101. Bowlas, Christopher J.; Bruce, Duncan W.; Seddon, Kenneth R. *Chem. Commun.* **1996**, 1625-1626.
102. Gordon, Charles M. ; Holbrey, John D. ; Kennedy, Alan R.; Seddon, Kenneth R. *J. Mater. Chem.* **1998**, 8, 2627-2636.
103. Holbrey, John D.; Seddon, Kenneth R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133-2139.
104. Oyumi, Y.; Brill, T.; Rheingold, A.; Lowe-Ma, C. *J. Phys. Chem.* **1985**, 89, 2309.
105. Bracuti, A. *J. Crystallogr. Spectrosc. Res.* **1993**, 23, 669.
106. Mylrajan, M.; Srinivasan, T.; Sreenivasamurthy, G. *J. Crystallogr. Spectrosc. Res.* **1985**, 15, 493.
107. Doxsee, K.; Francis, P.; Weakley, T. *Tetrahedron 2000*, 56, 6683.

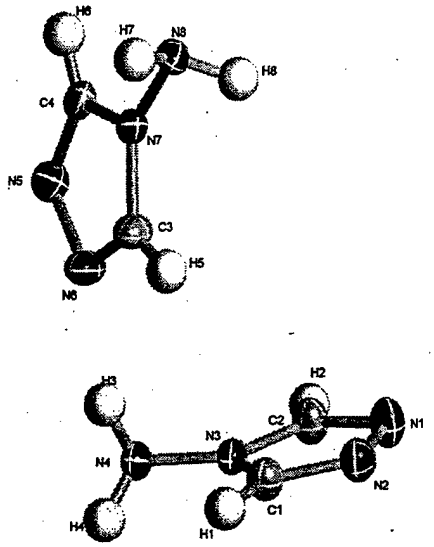


Figure 1. X-ray crystallography structure of 4-amino-1,2,4-triazole. The bond distances (Å) are: N(1)-N(2)=1.379(5); N(1)-C(2)=1.307(5); N(2)-C(1)=1.300(4); N(3)-N(4)=1.418(4); N(3)-C(1)=1.360(5); N(3)–C(2)=1.338(4); N(4)-H(3)=0.98(5); N(4)-H(4)=0.94(4); N(5)-C(4)=1.297(6); N(5)-N(6)=1.396(4); N(6)-C(3)=1.312(6); N(7)-C(4)=1.356(4); N(7)-N(8)=1.411(5); N(7)-C(3)=1.350(4); N(8)-H(7)=0.92(5); N(8)-H(8)=0.95(3); C(1)-H(1)=0.94(4); C(2)-H(2)=0.83(6); C(3)-H(5)=0.94(3); C(4)-H(6)=0.89(4).

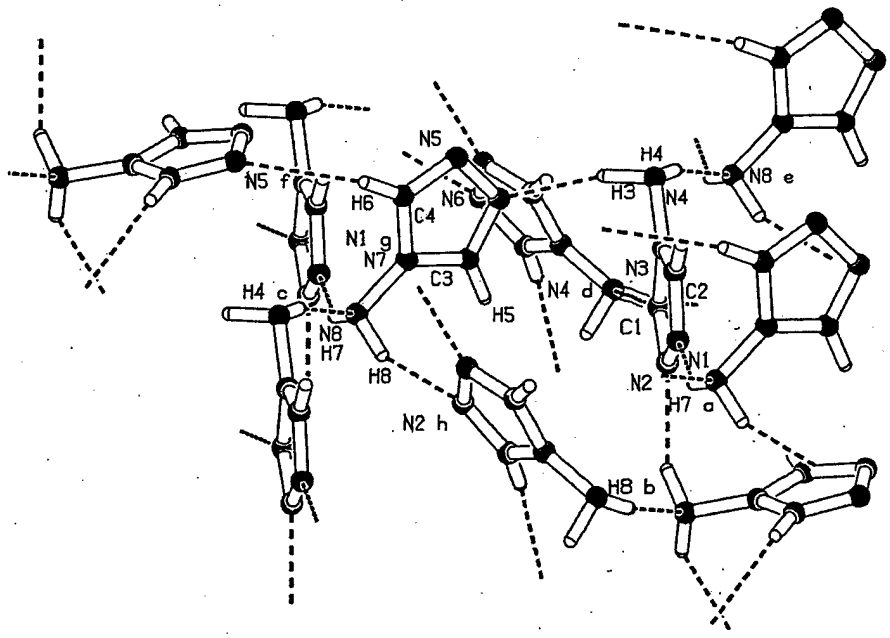


Figure 2. Structure showing significant hydrogen bonds of 4-amino-1,2,4-triazole. The interatomic distance (Å) and symmetry code are: N(8)..H(3)=2.05(5), x,y,z; n(8) e..H(4)=2.10(4), x, y, -1+z; N(1)..H(7) a=2.19, -1/2+x, ½+y,z; N(1) g..H(8)=2.70(5), x, 1-y, ½+z; N(2)..H(8) b=2.03(4), x, 1-y, ½+z; N(4) d..H(1)=2.51(4), -1/2+x, 3/2-y, -1/2+z; N(5) f..H(6)=2.56(4), x, 2-y, ½+z; N(6) f..H(6)=2.69(4), x, 2-y, ½+z.

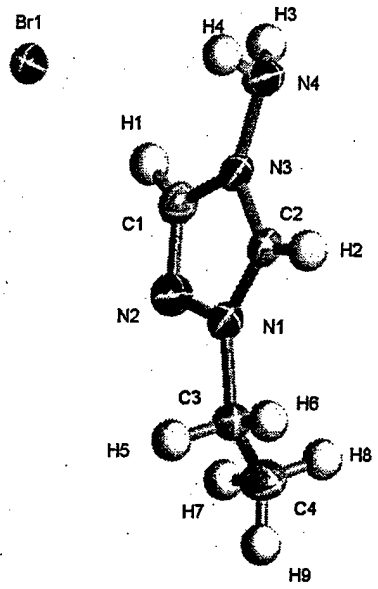


Figure 3. X-ray crystallography structure of 1-ethyl-4-amino-1,2,4-triazolium bromide (II). The bond distances (Å) are: N(1)-N(2)=1.369(2); N(1)-C(2)=1.312(2); N(1)-C(3)=1.480(2); N(2)-C(1)=1.310(2); N(3)-N(4)=1.419(2); N(3)-C(1)=1.356(3); N(3)-C(2)=1.337(2); N(4)-H(3)=0.92(2); N(4)-H(4)=0.83(2); C(3)-C(4)=1.502(3); C(1)-H(1)=0.99(3); C(2)-H(2)=0.94(3); C(3)-H(5)=0.98(3); C(3)-H(6)=0.84(2); C(4)-H(7)=0.89(2); C(4)-H(8)=0.98(3); C(4)-H(9)=0.95(3).

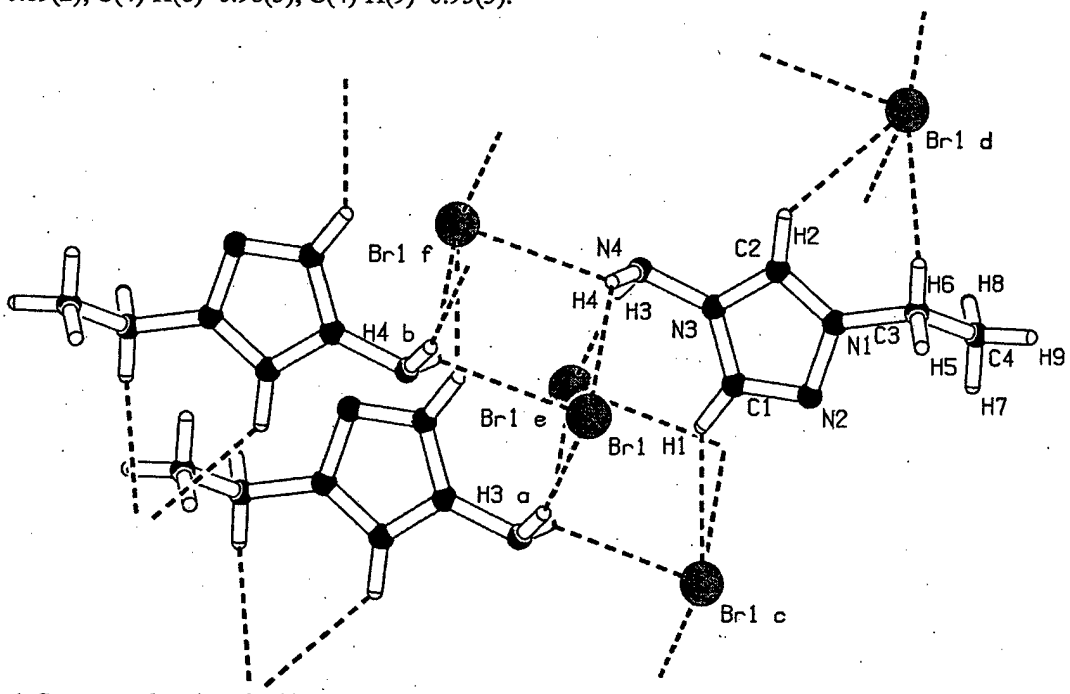


Figure 4. Structure showing significant cation-anion contacts of 1-ethyl-4-amino-1,2,4-triazolium bromide (II). The interatomic distance (Å) and symmetry code are: Br(1)..H(3) a=2.53(2), -x, -y, 1-z; Br(1)..H(4)= 2.89(2), x, y, z; Br(1) f..H(4)= 2.84(2), x-1, -y, 2-z; Br(1) c..H(1)= 2.77(3), -1+x, y, z; Br(1) d..H(2)= 2.89(3), x, y, 1+z; Br(1) d..H(6)= 3.00(2), x, y, 1+z.

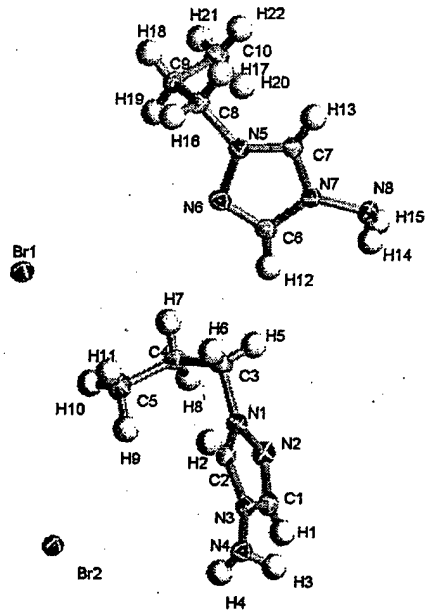


Figure 5. X-ray crystallography structure of 1-propyl-4-amino-1,2,4-triazolium bromide (III). The bond distances (Å) are: N(1)-N(2)=1.373(3); N(1)-C(2)=1.307(3); N(1)-C(3)=1.470(3); N(2)-C(1)=1.307(4); N(3)-N(4)=1.414(3); N(3)-C(1)=1.364(4); N(3)-C(2)=1.329(3); N(4)-H(4)=0.79(3); N(4)-H(3)=0.87(3); N(5)-C(7)=1.313(3); N(5)-C(8)=1.466(3); N(5)-N(6)=1.374(3); N(6)-C(6)= 1.300(3); N(7)-C(6)=1.365(3); N(7)-C(7)=1.328(3); N(7)-N(8)=1.418(3); N(8)-H(15)=0.87(3); N(8)-H(14)=0.87(3); C(3)-C(4)=1.514(3); C(4)-C(5)=1.524(4); C(1)-H(1)=0.87(3); C(2)-H(2)=0.92(3); C(3)-H(5)=0.92(4); C(3)-H(6)=0.93(3); C(4)-H(7)=0.92(3); C(4)-H(8)=0.98(3); C(5)-H(10)=1.00(3); C(5)-H(9)=1.02(3); C(5)-H(11)=0.89(4); C(8)-C(9)=1.515(4); C(9)-C(10)=1.514(4); C(6)-H(12)=0.96(3); C(7)-H(13)=0.92(3); C(8)-H(16)=0.94(3); C(8)-H(17)=0.98(3); C(9)-H(18)=0.92(3); C(9)-H(19)=0.96(3); C(10)-H(20)=0.99(3); C(10)-H(21)=0.98(3); C(10)-H(22)=0.96(3).

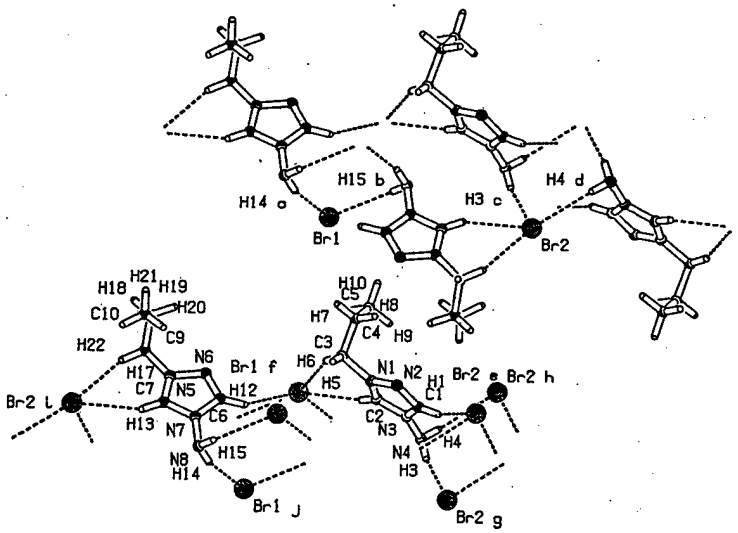


Figure 6. Structure showing significant cation-anion contacts of 1-propyl-4-amino-1,2,4-triazolium bromide (III). The interatomic distance (Å) and symmetry code are: Br(2) g..H(3)= 2.57(3), x, -1+y, z; Br(2) h..H(4)= 2.71(3), 1-x, 1-y, -z; Br(1)..H(14) a= 2.54(3), x, -1+y, z; Br(1)..H(15) b= 2.71(3), 2-x, 1-y, 1-z; Br(2) e..H(1)= 2.91(3), 2-x, 1-y, -z; Br(1) f..H(2)= 2.64(3), 1-x, 1-y, 1-z; Br(1) f..H(6)= 2.91(3), 1-x, 1-y, 1-z; Br(1) f..H(12)= 2.99(3), 1-x, 1-y, 1-z; Br(2) i..H(13)= 2.66(3), 2-x, 1-y, 1-z; Br(2) i..H(17)= 2.95(3), 2-x, 1-y, 1-z.

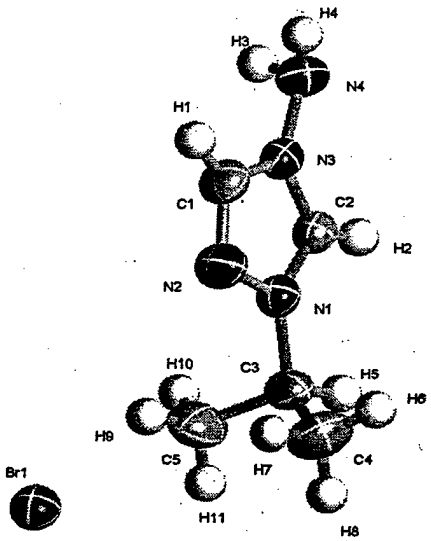


Figure 7. X-ray crystallography structure of 1-isopropyl-4-amino-1,2,4-triazolium bromide (IV). The bond distances (Å) are: N(1)-N(2)=1.361(3); N(1)-C(2) =1.298(3); N(1)-C(3)=1.477(3); N(2)-C(1)=1.297(3); N(3)-N(4)=1.400(3); N(3)-C(1)=1.355(3); N(3)-C(2)=1.327(3); N(4)-H(4)=0.92(4); N(4)-H(3)=0.86(3); C(3)-C(5)=1.504(5); C(3)-C(4)=1.500(4); C(1)-H(1)=0.92(3); C(2)-H(2)=0.90(3); C(3)-H(5)=1.00(3); C(4)-H(6)=0.96(4); C(4)-H(7)=0.96(5); C(4)-H(8)=0.95(5); C(5)-H(9)=0.96(5); C(5)-H(10)=0.96(5); C(5)-H(11)=0.92(5).

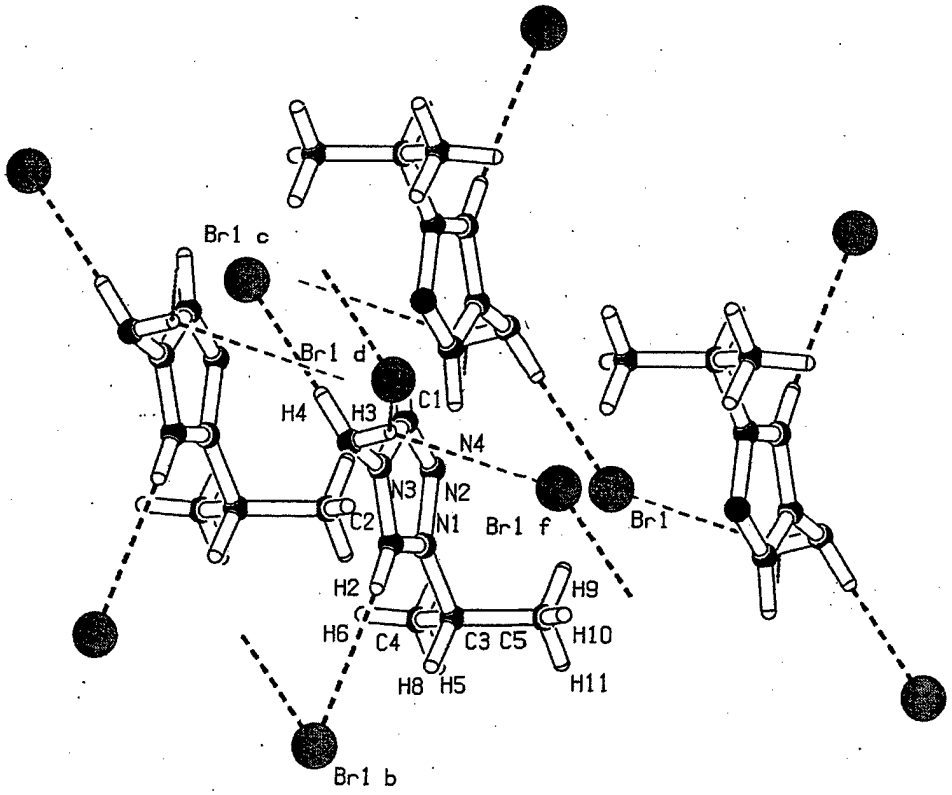


Figure 8. Structure showing significant cation-anion contacts of 1-isopropyl-4-amino-1,2,4-triazolium bromide (IV). The interatomic distance (Å) and symmetry code are: Br(1) c..H(4)= 2.50(4), -x, 2-y, 1-z; Br(1) d..H(3)= 2.98(3), x, 1+y, 1+z; Br(1) f..H(3)= 2.96(3), 1-x, 2-y, 1-z; Br(1) b..H(2)= 2.79(3), x, y, 1+z; Br(1) b..H(5)= 2.95(3), x, y, 1+z.

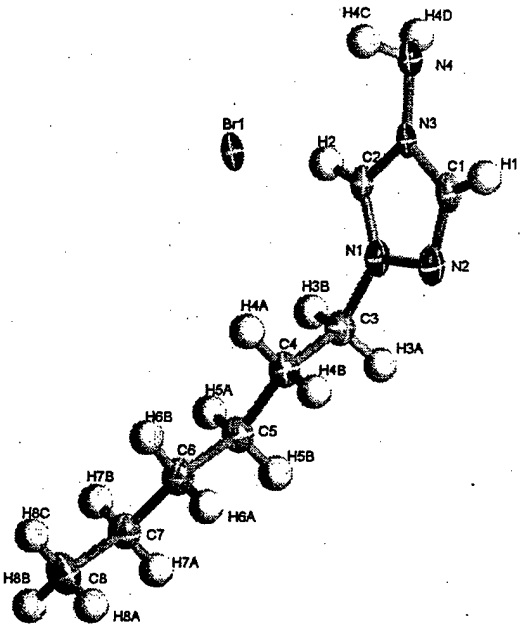


Figure 9. X-ray crystallography structure of 1-hexyl-4-amino-1,2,4-triazolium bromide (VIII). The bond distances (Å) are: N(1)-N(2)=1.373(3); N(1)-C(2)=1.308(4); N(1)-C(3)=1.456(4); N(2)-C(1)=1.293(4); N(3)-N(4)=1.394(4); N(3)-C(1)=1.350(4); N(3)-C(2)=1.334(4); N(4)-H(4D)=0.81(4); N(4)-H(4C)=0.93(3); C(3)-C(4)=1.514(4); C(4)-C(5)=1.529(4); C(5)-C(6)=1.526(5); C(6)-C(7)=1.504(5); C(7) –C(8)=1.531(5); C(1)-H(1)= 0.9304; C(2)-H(2)=0.9298; C(3)-H(3A)=0.9705; C(3)-H(3B)=0.9702; C(4)-H(4A)=0.9698; C(4)-H(4B)= 0.9701; C(5)-H(5A)=0.9697; C(5)-H(5B)=0.9704; C(6)-H(6A)= 0.9708; C(6)-H(6B)=0.9692; C(7)-H(7A)=0.9702; C(7)-H(7B)=0.9697; C(8)-H(8A)=0.9598; C(8)-H(8B)=0.9599; C(8)-H(8C)=0.9590.

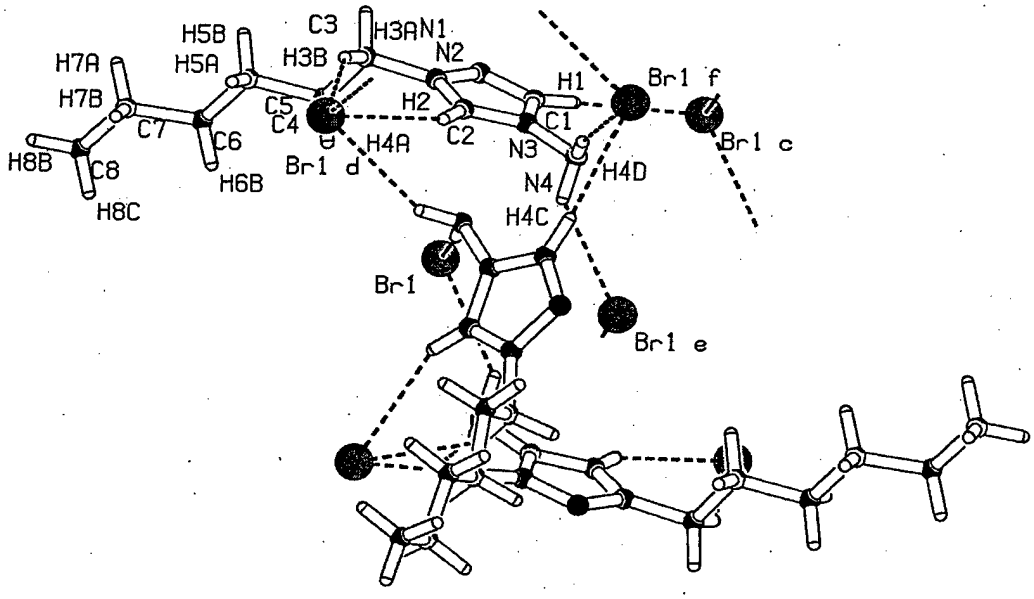


Figure 10. Structure showing significant cation-anion contacts of 1-hexyl-4-amino-1,2,4-triazolium bromide (VIII). The interatomic distance (Å) and symmetry code are: Br(1) e..H(4C)= 2.73(3), 1-x, 1-y, -z; Br(1) f..H(4D)= 2.66(4), 1-x, -½+y, ½-z; Br(1) c..H(1)= 2.7300, x, -1+y, z; Br(1) d..H(2)= 2.7600, x, 3/2-y, ½+z; Br(1) d..H(3B)= 2.8500, x, 3/2-y, ½+z.

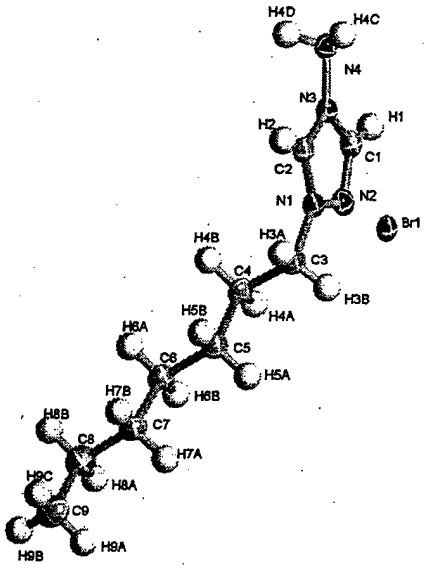


Figure 11. X-ray crystallography structure of 1-heptyl-4-amino-1,2,4-triazolium bromide (IX). The bond distances (Å) are: N(1)-N(2)=1.377(3); N(1)-C(2)=1.314(4); N(1)-C(3)=1.464(4) N(2)-C(1)=1.303(4); N(3)-N(4)=1.401(3); N(3)-C(1)=1.357(4); N(3)-C(2)=1.333(3); N(4)-H(4D)=0.90(4); N(4)-H(4C)=0.80(5); C(3)-C(4)=1.516(5); C(4)-C(5)=1.529(4); C(5)-C(6)=1.526(4); C(6)-C(7)=1.524(4); C(7)-C(8)=1.513(4); C(8)-C(9)=1.531(5); C(1)-H(1)=0.9498; C(2)-H(2)=0.9498; C(3)-H(3A)=0.97(4); C(3)-H(3B)=0.91(3); C(4)-H(4A)=0.9905; C(4)-H(4B)=0.9907; C(5)-H(5A)=0.9896; C(5)-H(5B)=0.9903; C(6)-H(6A)=0.9899; C(6)-H(6B)=0.9893; C(7)-H(7A)=0.9906; C(7)-H(7B)=0.9903; C(8)-H(8A)=0.9897; C(8)-H(8B)=0.9904; C(9)-H(9A)=0.9802; C(9)-H(9B)=0.9793; C(9)-H(9C)=0.9795.

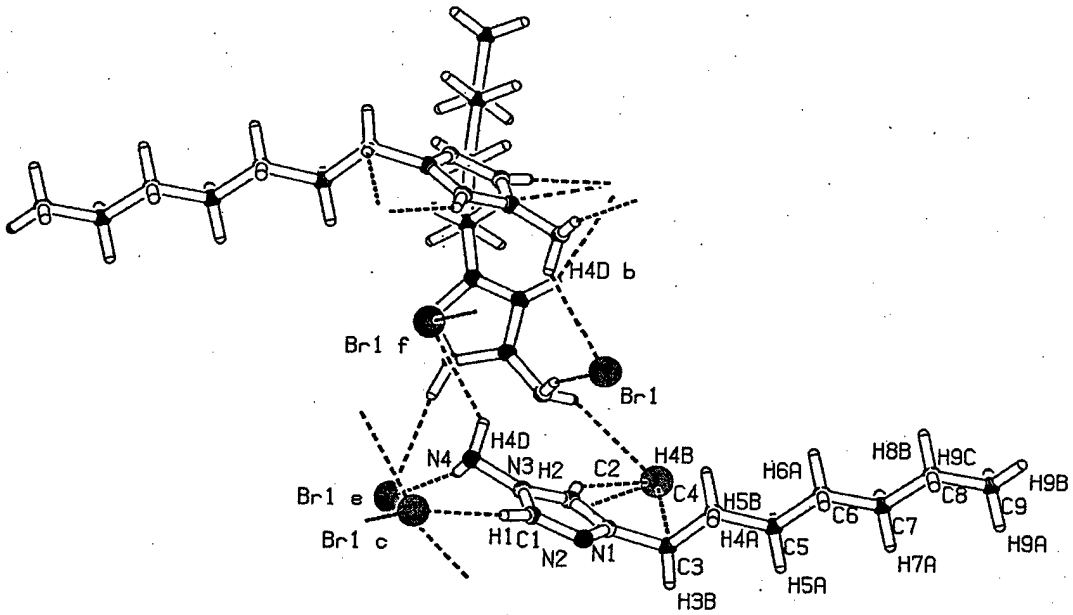


Figure 12. Structure showing significant cation-anion contacts of 1-heptyl-4-amino-1,2,4-triazolium bromide (IX). The interatomic distance (Å) and symmetry code are: Br(1) e..H(4C)= 2.66(4), 1-x, -1/2+y, 3/2-z; Br(1) f..H(4D)= 2.77(4), 1-x, 1-y, 2-z; Br(1) c..H(1)= 2.7100, x, -1+y, z; Br(1) d..H(2)= 2.7900, x, 3/2-y, -1/2+z; Br(1)..H(3A)= 2.85(3), x, 3/2-y, ½+z.

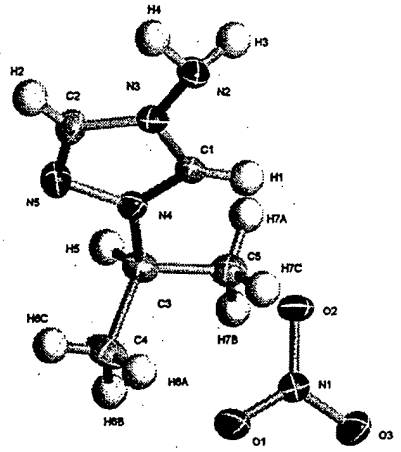


Figure 13. X-ray crystallography structure of 1-isopropyl-4-amino-1,2,4-triazolium nitrate (XVIII). The bond distances (Å) are: O(1)-N(1)=1.241(3); O(2)-N(1)=1.255(3); O(3)-N(1)=1.254(3); N(2)-N(3)=1.415(3); N(3)-C(1)=1.338(3); N(3)-C(2)=1.354(3); N(4) –N(5)=1.363(3); N(4)-C(1)=1.316(3); N(4)-C(3)=1.484(3); N(5)-C(2)=1.305(4); N(2)-H(3)=0.90(3); N(2)-H(4)=0.92(4); C(3)-C(5)=1.509(3); C(3)-C(4)=1.517(4); C(1)-H(1)=0.9294; C(2)-H(2)=0.9299; C(3)-H(5A)=0.9804; C(4)-H(6C)=0.9600; C(4)-H(6A)=0.9598; C(4)-H(6B)=0.9602; C(5)-H(7A)=0.9597; C(5)-H(7B)=0.9600; C(5)-H(7C)=0.9599.

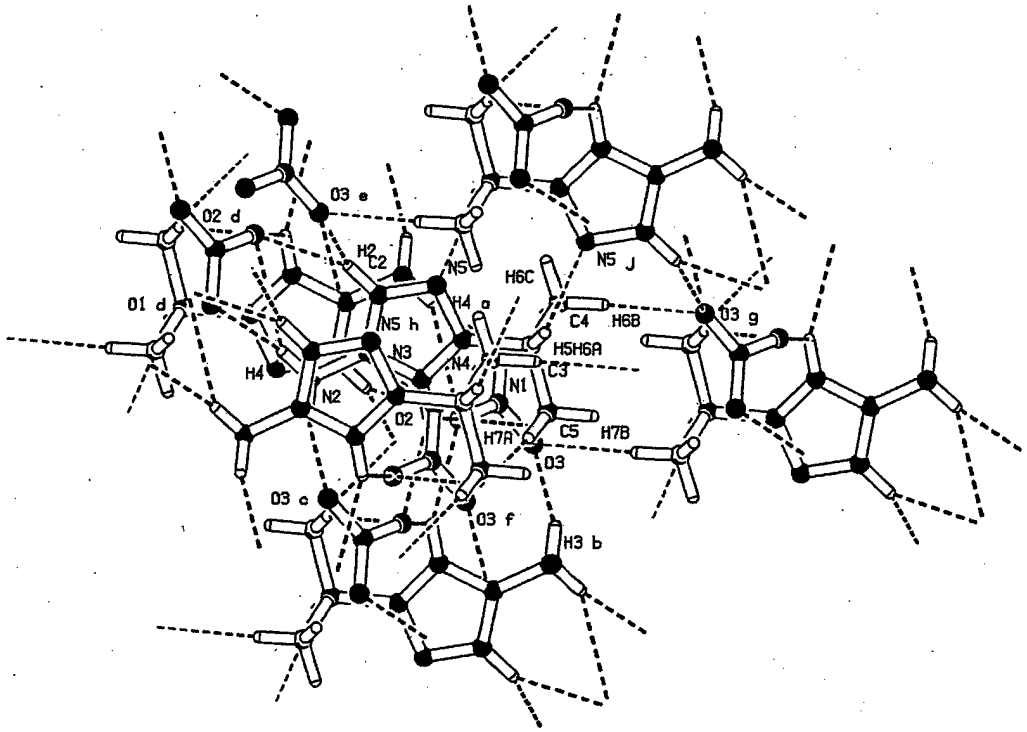


Figure 14. Structure showing significant cation-anion contacts of 1-isopropyl-4-amino-1,2,4-triazolium nitrate (XVIII). The interatomic distance (Å) and symmetry code are: O(3) c..H(3)= 2.11(3), 1-x,1-y,-z; O(1) d..H(4)= 2.08(4), 2-x,1-y,-z; O(2) d..H(4)= 2.62(4), 2-x,1-y,-z; O(2)..H(1)= 2.4700, x, y, z; O(2) c..H(1)= 2.3200, 1-x,1-y,-z; O(3) e..H(2)= 2.3900, 1+x,1+y,z; O(2) d..H(2)= 2.4300, 2-x,1-y,-z; N(5) j..H(5)= 2.6600, 2-x,2-y,1-z; O(3) g..H(6B)= 2.6300, 1-x,1-y,1-z; O(3) f..H(7A)= 2.6900, x,1+y,z; O(2)..H(7C)= 2.6900, x, y, z.

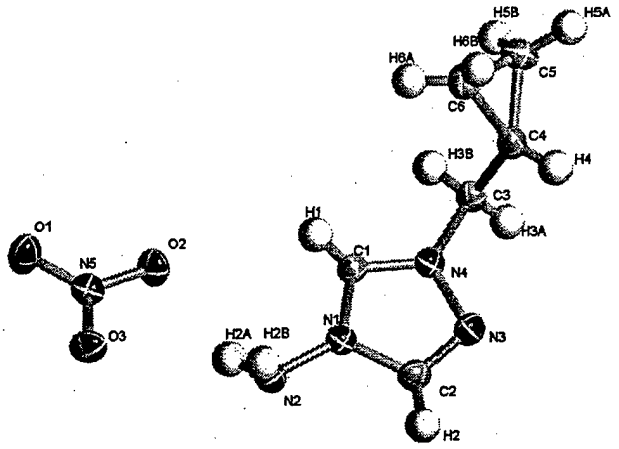


Figure 15. X-ray crystallography structure of 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate (XX). The bond distances (Å) are: O(1)-N(5)=1.234(2);O(2)-N(5)=1.266(2); O(3)-N(5)=1.249(2); N(1)-C(2)=1.354(2); N(1)-N(2)=1.401(2); N(1)-C(1)=1.332(2); N(3)-N(4)=1.366(2); N(3)-C(2)=1.303(2); N(4)-C(1)=1.310(2); N(4)-C(3)=1.466(2); N(2)-H(2A)=0.89(2); N(2)-H(2B)=0.88(2); C(3)-C(4)=1.497(2); C(4)-C(6)=1.500(2); C(4)-C(5)=1.500(2); C(5)-C(6)=1.496(2); C(1)-H(1)=0.87(2); C(2)-H(2)=0.94(2); C(3)-H(3A)=0.96(2);C(3)-H(3B)=0.97(2); C(4)-H(4) = 0.95(2); C(5)-H(5A)=0.98(2);C(5)-H(5B)=0.95(2); C(6)-H(6A)=0.95(2); C(6)-H(6B)=0.97(2).

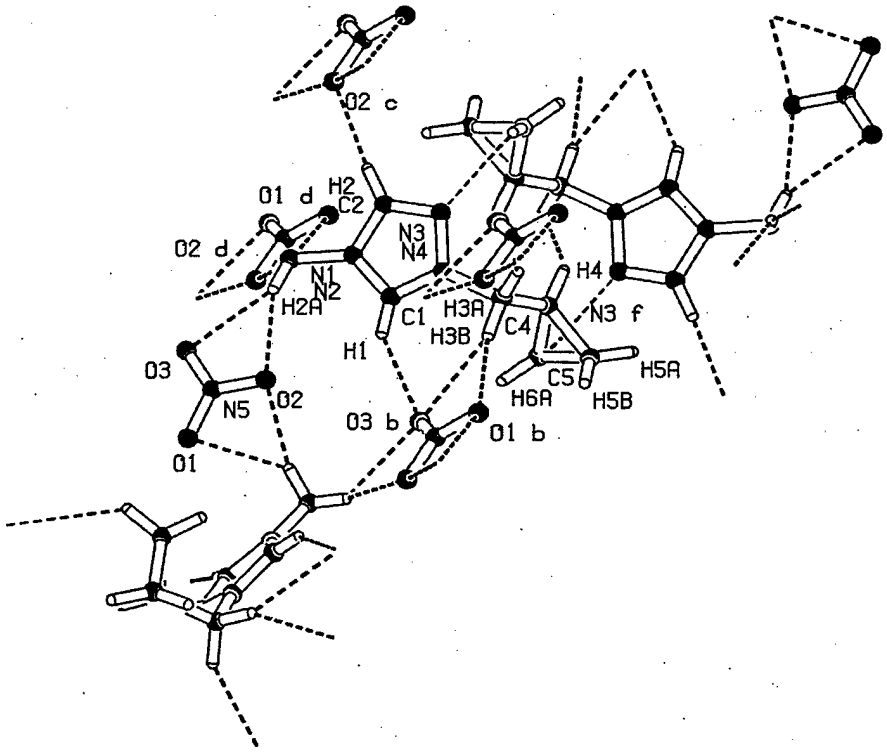


Figure 16. Structure showing significant cation-anion contacts of 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate (XX). The interatomic distance (Å) and symmetry code are: O(2)..H(2A)=2.18(2), x, y, z; O(3)..H(2A)=2.39(2), x, y, z; O(1) d..H(2B)=2.39(2), 1/2-x, -1/2+y, 3/2-z; O(2) d..H(2B)=2.12(2), 1/2-x, -1/2+y, 3/2-z; O(3) b..H(1)=2.42(2), 1/2-x, 1/2+y, 3/2-z; O(2) c..H(2)=2.20(2), 3/2-x, -1/2+y, 3/2-z; O(3) e..H(3A)=2.44(2), 3/2-x, -1/2+y, 3/2-z; O(1) b..H(3B)=2.53(2), 1/2-x, 1/2+y, 3/2-z; O(3) b..H(3B)=2.45(2), 1/2-x, 1/2+y, 3/2-z; N(3) f..H(6B)=2.73(2), 2-x, 2-y, 2-z.

Table 1. Physical properties of 1-R-4-amino-1,2,4-triazolium bromides.

Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm^3)
1-methyl (I-)	92	135	1.98
1-ethyl	67	130	1.69
1-n-propyl	63	120	1.56
1-isopropyl	92	110	1.60
1-allyl	62	130	1.59
1-butyl	48	130	1.46
1-methylcyclopropyl	73	150	1.58
1-n-pentyl	54	130	1.37
1-n-hexyl	76	120	1.34
1-n-heptyl	94	120	1.30
1-n-octyl	80	135	1.27
1-n-nonyl	81	140	1.26
1-n-decyl	90	135	1.23

Table 2. Physical properties of 1-R-4-amino-1,2,4-triazolium nitrates.

Salt	melting point(°C)	decomp onset(°C)
1-methyl	-54(g)	175
1-ethyl	-55(g)	160
1-n-propyl	33	175
1-isopropyl	66	180
1-(2-propenyl)	-50(g)	140
1-n-butyl	-50 (g)	170
1-methylcyclopropyl	56	185
1-n-pentyl	29	180
1-n-hexyl	0	170
1-n-heptyl	35	165
1-n-octyl	34	165
1-n-nonyl	53	175
1-n-decyl	51	185

Table 3. Crystal Data and Details of the Structure Determination.

Crystal Data						
Chemical Name	4-Amino-1,2,4-Triazole	Ethyl	n-Propyl	Isopropyl	n-Hexyl	n-Heptyl
Formula	C2 H4 N4	C4 H9 N4, Br	C5 H11 N4, Br	C5 H11 N4, Br	C8 H17 N4, Br	C9 H19 N4, Br
Formula Weight	84.09	193.05	207.08	207.08	249.16	263.18
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	Cc (No. 9)	P21/n (No. 14)	P-1 (No. 2)	P-1 (No. 2)	P21/c (No. 14)	P21/c (No. 14)
a [Å]	11.94(2)	5.117(2)	5.1237(7)	6.4138(9)	19.131(5)	20.914(4)
b [Å]	10.79(1)	18.439(5)	10.943(1)	7.633(1)	6.314(2)	6.422(1)
c [Å]	8.28(1)	7.846(2)	15.681(2)	8.709(1)	9.611(2)	9.505(2)
α [deg]	90	90	105.777(2)	94.446(2)	90	90
β [deg]	133.23(2)	98.371(5)	92.264(2)	92.170(2)	98.567(4)	95.602(3)
γ [deg]	90	90	99.091(2)	97.807(2)	90	90
V [Å**3]	777(2)	732(3)	832.3(2)	420.6(1)	1148.0(5)	1270.4(4)
Z	8	4	4	2	4	4
D(calc) [g/cm**3]	1.437	1.751	1.653	1.635	1.442	1.376
μ(MoKa) [/mm]	0.107	5.533	4.875	4.822	3.547	3.210
F(000)	352	384	416	208	512	544
Crystal Size [mm]	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00
Data Collection						
Temperature (K)	100	RT	100	RT	RT	100
Theta Min-Max [Deg]	3.0, 25.4	2.8, 28.3	1.4, 25.4	2.7, 26.4	2.2, 25.4	2.0, 25.4
Dataset	-12: 14 ; -9: 12 ; -9: 9	-6: 6 ; -24: 23 ; -10: 7	-6: 5 ; -13: 13 ; -18: 16	-8: 5 ; -9: 9 ; -10: 10	-23: 22 ; -7: 7 ; -11: 9	-23: 25 ; -4: 7 ; -11: 10
Tot., Uniq. Data, R(int)	1753, 1201, 0.030	4423, 1688, 0.027	4468, 2989, 0.015	2349, 1676, 0.022	5751, 2117, 0.034	6313, 2326, 0.032
Observed data [I > 2.0 σ(I)]	1155	1557	2746	1600	1824	2086
Refinement						
Nref, Npar	1201, 142	1688, 119	2989, 269	1676, 136	2117, 127	2326, 144
R, wR2, S	0.0412, 0.1128, 1.05	0.0261, 0.0722, 1.03	0.0269, 0.0774, 1.09	0.0272, 0.0701, 1.06	0.0410, 0.1091, 1.04	0.0428, 0.1258, 1.06
where P= Fo^2^+2Fc^2^)/3	w = 1/[\s^2^(Fo^2^) +(0.0874P)^2^]		w = 1/[\s^2^(Fo^2^) +(0.0556P)^2^+0.0865P]	w = 1/[\s^2^(Fo^2^) +(0.0406P)^2^+0.1045P]	w = 1/[\s^2^(Fo^2^) +(0.0797P)^2^]	w = 1/[\s^2^(Fo^2^ +(0.0993P)^2^
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00	0.00, 0.00	0.00, 0.00	0.00, 0.00	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-0.29, 0.25	-0.60, 0.73	-0.71, 0.88	-0.52, 0.47	-0.64, 7.92	-0.86, 1.54

Table 3 (cont.). Crystal data and details of collection.

Crystal Data		
Chemical Name	1-Isopropyl-NO3	1-Methylcyclopropyl NO3
Formula	C5 H11 N4, N O3	C6 H11 N4, N O3
Formula Weight	189.19	201.20
Crystal System	Triclinic	Monoclinic
Space group	P-1 (No. 2)	P21/n (No. 14)
a [Å]	7.018(3)	5.402(3)
b [Å]	7.176(3)	8.526(4)
c [Å]	9.100(4)	20.255(9)
α [deg]	106.426(6)	90
β [deg]	91.865(7)	97.317(8)
γ [deg]	93.224(7)	90
V [Å**3]	438.3(3)	925.3(8)
Z	2	4
D(calc) [g/cm**3]	1.434	1.444
μ(MoKa) [/mm]	0.119	0.117
F(000)	200	424
Crystal Size [mm]	0.00 x 0.00 x 0.00	0.00 x 0.00 x 0.00
Data Collection		
Temperature (K)	100	100
Theta Min-Max [Deg]	2.3, 25.4	2.0, 25.5
Dataset	-8: 4 ; -7: 8 ; -10: 9	-6: 6 ; -10: 7 ; -24: 23
Tot., Uniq. Data, R(int)	1641, 1343, 0.015	4718, 1695, 0.029
Observed data [I > 2.0 σ(I)]	1234	1530
Refinement		
Nref, Npar	1343, 129	1695, 171
R, wR2, S	0.0562, 0.1787, 1.15	0.0331, 0.0904, 1.05
where P= (Fo^2^+2Fc^2^)/3	w = 1/[\s^2^(Fo^2^)+ (0.1139P)^2^+0.2471P]	w = 1/[\s^2^(Fo^2^)+ (0.0513P)^2^+0.2126P]
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-0.30, 0.29	-0.24, 0.20